

MINISTRY OF THE ENVIRONMENT

MAY 19 1981

HAZARDOUS CONTAMINANTS
OFFICE

CONFERENCE PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE NO. 1

Skyline Hotel, Toronto, Ontario

November 25, 1980

RESEARCH ADVISORY COMMITTEE

Ministry of the Environment

Province of Ontario



Ministry
of the
Environment

The Honourable
Keith C. Norton, Q.C.,
Minister

Graham W. S. Scott, Q.C.,
Deputy Minister

TD
1725
057
1980

CONFERENCE PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE NO. 1

Skyline Hotel, Toronto, Ontario
November 25, 1980

RESEARCH ADVISORY COMMITTEE
Ministry of the Environment
Province of Ontario



Ontario

Ministry
of the
Environment

The Honourable
Harry C. Parrott, DDS
Minister

Graham W. S. Scott, QC
Deputy Minister

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

TABLE OF CONTENTS

<u>Title of Paper</u>	<u>Speaker</u>	<u>Affiliation</u>	<u>Page</u>
Environmental Effects of Waste Oil as a Road Dust Suppressant	F. Guillaume	L. S. Love and Associates Canada Ltd. 158 Kennedy Road, South Brampton, Ontario L6W 3G7	1
The Effects of Road Oiling on PCB Accumulation in Aquatic Life	K. Suns	Water Resources Branch	19
Waste Oil Utilization	E. W. Turner	Waste Management Branch	37
Bio-accumulation Rates, Acute and Chronic Effects of New Dielectric Fluid Products on Fish	G. W. Ozburn	Lakehead University Department of Biology Thunder Bay, Ontario P7B 5E1	49
Factors Affecting the Accumulation of Organics in Fish	G. R. Craig	Water Resources Branch	92
The Problem of Abandoned Mines in Ontario - A Confrontation with History	J. E. Duignan	Waste Management Branch	94
Methodology for Developing a Quantity and Location Inventory of Hazardous Compounds in Ontario	K. R. Ashwood	Acres Consulting Services Ltd. 5259 Dorchester Road Niagara Falls, Ontario L2E 6W1	113
Ontario's Seven Point Program for Liquid Industrial Waste Disposal	P. Isles	Waste Management Branch	124
Environmental Impairment Liability Insurance	G.T.G. Scott	Geoffrey T. G. Scott Consulting Engineer Suite 201 801 York Mills Road Don Mills, Ontario M3B 1X7	146
Subsurface Contaminant Migration from Landfills - Research Results	J. A. Cherry	University of Waterloo Faculty of Science Waterloo, Ontario N2L 3G1	155
Organic Contaminant Removal in Drinking Water - An Overview	K. J. Roberts	Pollution Control Branch	175
Organic Contaminant Removal in Drinking Water - Field Experiences	R. B. Hunsinger	Pollution Control Branch	198

Table of Contents (cont'd.)

<u>Title of Paper</u>	<u>Speaker</u>	<u>Affiliation</u>	<u>Page</u>
Viruses and the Environment	G. Jenkins	Laboratory Services Branch	212
An Application of Thermal Sensing Techniques	W. Bernert	Intertech Remote Sensing Ltd. P.O. Box 507, R.R. #5 Hunt Club Road Ottawa, Ontario K1G 3N3	234
The Pickering "A" Thermal Plume During Winter Months. Some Preliminary Results from a Co-operative Study	R. R. Weiler	Water Resources Branch	243
The Uptake of Methyl-mercury by Walleye through a Simulated Ecosystem as a Function of Selected pH Regimes	T. A. Watson	J. F. MacLaren Ltd. 1220 Sheppard Avenue E. Suite 100 Willowdale, Ontario M2K 2T8	264
Atmospheric Deposition of Mercury in Ontario	N. D. Johnson	Ontario Research Foundation Sheridan Park Research Community Mississauga, Ontario L5K 1B3	297
Event Precipitation Samplers or Use in Acid Rain Studies	D. M. Kane	United Technology and Science Inc. 75 Eglinton Avenue E. Toronto, Ontario M4P 1H3	322
Definition of the Sphere of Influence of the Mining Activities at Elliot Lake, Ontario by Assessment of the Levels of Uranium and Other Elements in Lichens and Mosses	E. Nieboer	McMaster University Department of Bio-chemistry Health Sciences Centre 1200 Main Street W. Hamilton, Ontario L8S 4J9	343
Acid Rain - An Overview of the Ontario Program	E. W. Piche	Ministry of the Environment	366

INTRODUCTION

Ministry of the Environment
Province of Ontario

Technology Transfer Conference No. 1
Tuesday, November 25, 1980

Skyline Hotel
655 Dixon Road
Rexdale, Toronto
Ontario M9W 1J4

Featuring Completed Research Projects
Supported by the Provincial Lottery
Trust Fund

Sponsored and presented by the
Research Advisory Committee
Ministry of the Environment

The Research Advisory Committee, Ontario Ministry of the Environment sponsored Technology Transfer Conference No. 1 on November 25, 1980 at the Skyline Hotel for the purpose of distributing information arising from Provincial Lottery Research Projects and from other selected M.O.E. in-house and external research projects. At this conference, Contractors, Principal Investigators, Liaison Officers and Researchers described and discussed results of their projects giving emphasis to useful applications of the investigational work.

The attendance at this one day session was divided between two parallel sessions of their choice. The program was structured for M.O.E. Staff and Researchers, Ontario and Federal Government Personnel, Consultants, Contractors, University Personnel, Industry Representatives and Media.

Twenty papers were given at the Conference and of these, thirteen were supported with Provincial Lottery Trust Funds.

ACKNOWLEDGEMENT

This Conference Proceedings is issued to describe environmental oriented research projects conducted by the Ontario Government, assisted by the Federal Government, Ontario Hydro, National Water Research Institute, Universities and the Private Sector. All initial enquiries regarding the papers given at the Conference should be made to the authors and speakers or to their affiliation.

DISCLAIMER

The contents of this Conference Proceedings have been reviewed by the Research Advisory Committee and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Ontario Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Session Chairmen at Conference No. 1:

D. A. McTavish,	Southwestern Region
B. I. Boyko,	Waste Management Branch
P. D. Foley,	Pollution Control Branch
G. C. Ronan,	Laboratory Services Branch

"ENVIRONMENTAL EFFECTS OF WASTE
OIL AS A ROAD DUST SUPPRESSANT".

by

F. Guillaume

L.S. Love and Associates Canada Ltd.
Brampton, Ontario.

FOR PRESENTATION AT THE
TECHNOLOGY TRANSFER CONFERENCE NO.1

November 25, 1980.

Skyline Hotel,

Rexdale, Ontario.

1. INTRODUCTION:

This paper will give a brief overview of a two-year study programme on the environmental effects of waste oil as a road dust suppressant. Detailed reports were prepared for presentation to the M.O.E. Waste Management Branch, after completion of the respective phases of the study.

The unsolicited proposal described the purpose of the study programme as follows: "To define the transport of oil and some of its components into the immediate environment of the road, i.e. dust, soil, vegetation and water, relative to an untreated section of road and a section which was treated with calcium chloride".

The potential difficulty of assessing the environmental effects was recognized, especially when these effects might be taken to include any adverse effects on wildlife, cattle, crops and humans. Clearly, a much broader study programme over an extended time period would be needed to attempt to evaluate those effects.

In our opinion a 1-year but preferably a two-year field study could provide some, if not most of the information required per the stated purpose for this study programme.

This study was undertaken by our Company on behalf of the Ministry of the Environment (MOE) and in conjunction with the Ministry of Transportation and Communications (MTC) who evaluated the physical characteristics of the treated roads and the observed effectiveness of dust control using the several dust suppressants.

During the summer and fall of 1977, four test roads were used in this study in Haldimand Township, Northumberland County, Ontario. During the 1978 phase two of these test roads were used again, while a third road was sampled only, without having been retreated with dust suppressants. During 1978 the sampling continued from mid-May to mid-November.

1. INTRODUCTION, (cont'd)

A key factor in the successful completion of all field activities during the study programme was the excellent co-operation we received from Mr. Tom McBride, Superintendent of Roads, Haldimand Township, in the selection and preparation of the test roads and his willing assistance throughout the 2-year study.

2. PROCEDURES AND METHODS:

The location of the four selected test roads in Haldimand Township is shown in Fig. No. 1. Road 1 was in east-west direction whereas roads 2, 3 and 4 were in a north-south position, so that the effect of wind direction on dust dispersion could be evaluated.

As shown in Fig. 1, both roads 1 and 2 crossed two small streams each, to permit an evaluation of any effects on nearby streams due to the dust suppressants.

The test roads had to be previously untreated gravel roads, approximately 1.6 km long, divided roughly into one third sections with the middle section as control separating the two treated sections, one with waste oil and the other with calcium chloride.

During the sampling programmes the Township Roads Superintendent had agreed to curtail the routine grading and maintenance of the test roads except for emergency attention as required, to correct severe potholing that had developed.

Proper selection of the test roads had to provide for adjacent shoulders and field areas suitable for soil sampling within a distance of 25 m from the road edge and also sufficient quantities of suitable types of vegetation in the shoulder areas.

For the 1978 phase of the study, roads 1 and 4 were selected for retreatment at the same sections as used in 1977, and a similar sampling programme was continued with the exception of vegetation and field soil. Road 3 was not retreated but was kept as a long term control with only road bed samples being taken on a once monthly basis.

2. PROCEDURES AND METHODS, (cont'd):

Application of waste oil for road dust control is usually in the range of 1-1.6 l/m² to an upper limit of 2.7 l/m². This is equivalent to a range of 0.2-0.29 lgal/Yd² and a limit of 0.5 lgal/Yd². The actual application rates during the study programme were in the range of 1.1-1.6 l/m², with some variation between the respective test roads and the two phases of the study programme.

The calcium chloride was applied as solid flakes in 1977 and as a liquid in 1978, at a rate of 2-2.3 kg/m (3½-4 ton/mile) per strip. This application rate was equivalent to 0.64-0.67 kg CaCl₂/m² of road surface. These application rates are normally used for dust control on rural roads.

At the start of the 1977 phase of the study, the CaCl₂ was applied to all test roads on June 17 and the application of the waste oil was made on June 22, in both cases the dates were selected depending on suitable weather conditions. During the 1978 phase of the work the field activities began earlier, with the CaCl₂ being applied on May 18 and the waste oil on May 24.

Traffic counters were installed on each test road to record the traffic density for the duration of each phase of the study programme.

Weather data were obtained from the monthly summary reports issued by the Peterborough weather station, supplemented as required by field observations. Of particular interest were the rainfall data and the effects of rainfall as a possible transport mechanism for the dust suppressants away from the road bed.

During 1977 the routine sampling programme included once-monthly sampling at each of the four test roads, of the road bed, shoulders, roadside vegetation and field soil. For the 1978 phase of the study, sampling was reduced to include only the road bed and shoulders on a bi-weekly basis at each of the two test roads. Samples of the road bed from road #3 were taken once monthly.

2. PROCEDURES AND METHODS, (cont'd):

The "Coning and Quartering" method of sampling dry materials was used for sampling the road bed, and later also the shoulder and field soil, in place of a hand-held core sampler which proved ineffective under the local soil conditions. The section to be sampled was loosened to a depth of 10 cm over an area of 30 x 30 cm. This loosened material was then subjected to the coning and quartering procedure. Generally 3 - 5 of these grab samples per test section constituted a single composite sample for subsequent chemical analysis. Field soil samples were taken for each section of test road at distances of 10 m, 15 m and 25 m from the edge of the road. All field soil samples were individual grab samples.

Sampling of the roadside vegetation included broadleaf plants and grasses, located in approximately the same area as the shoulder soil samples. The species of broadleaf plants and grasses chosen for sampling were based on the abundance of the respective plants and their respective growing seasons in the various sampling locations. The grass sample was always a mixture of the common field grasses at each location. The broadleaf plants varied from section to section and between the several test roads. The vegetation sample always represented several plants or parts of several plants within the selected sampling area.

Dust sampling was an integral part of the study programme during both the 1977 and 1978 phases. The main intention was to obtain an estimate of the quantity of settleable dust, within a reasonable distance from the edge of the road, e.g. 5m. The sampling procedure may be considered as a modification of the standard ASTM procedure for the collection of particulate atmospheric fall-out ASTM designation D1739-70. The individual sampling devices were standard mason jars placed approximately 55cm above grade and at a distance of 5m from the edge of the road along both sides of each test section. The exposure time was 1 week at the end of which clean jars were placed in the respective holders. At road No.4 these dust collectors were set up at distances of 5m, 10m and 25m from the edge of the road on both the east and the west sides of each test section.

At the control section of Road 4 two standard type ASTM dust collectors were installed in accordance with the procedure D1739-70. These units were placed 5m from the edge of the road with the mouth of the cylinder 2.4m above grade. In accordance with the ASTM procedure the dust collectors were left in the field for consecutive periods of 1 month.

2. PROCEDURES AND METHODS, (cont'd):

During 1978 two high volume air samplers were used to obtain samples of the suspended particulate in sufficient quantity to permit chemical analysis of the collected dust. Two high volume samplers were installed on Road 1, 5m from the edge of the road: One sampler on the north side of the oil section and the other on the south side of the CaCl_2 section.
2

Both roads 1 and 2 were traversed by two small fast flowing streams, one each respectively in the oil section and in the CaCl_2 section of each road. Each stream was inspected regularly for any evidence of run-off or leaching from the road bed, and water samples were taken upstream and downstream of the road in each location during or immediately after each heavy rainfall.

Samples of run-off water from the road bed were collected at every opportunity during sufficiently heavy rains, near the point where the run-off water left the road edge and entered the ditch or the road shoulder.

On a non-routine basis samples were taken of miscellaneous items such as oil coated stones which had been thrown on to the shoulder by passing cars, gravel that had been washed off the road, and run-off fines taken from the ditches and adjacent fields. These non-routine samples were to serve as evidence that measurable amounts of dust suppressant had left the road bed.

Chemical analysis was made routinely for lead and oil (as HEM, hexane extractable material) to indicate the possible presence of waste oil, and for chlorides to show possible traces of CaCl_2 . As necessary, control samples were analyzed for all three parameters.

Samples of waste oil as applied were analyzed for HEM, specific gravity, and the following heavy metals, arsenic, cadmium, chromium, copper, lead and zinc. Gas liquid chromatography was used to determine PCB's.

Samples of liquid CaCl_2 were analyzed for pH, specific gravity, chloride content and the presence of oil measured as HEM.

3. DISCUSSION OF OBSERVATIONS AND RESULTS:

As this presentation intends to be an overview of the completed work, this section will of necessity have to be a short summary of the total data and any pertinent discussion, to illustrate the more clearly evident trends in the data.

The 1977 phase of the programme showed the elusiveness of the 3 main parameters of interest, by confirming initial trends as variations of background concentrations rather than as significant trends. In part this was caused by the once monthly sampling programme and by sampling both field soil and roadside vegetation. It is for this reason that sampling of field soil and roadside vegetation was excluded from the 1978 programme. Besides, the summer of 1977 had above average rainfall in the study area, therefore requiring little help from dust suppressants to maintain reasonable control of dusty roads and producing somewhat inconclusive dustfall data.

Table 1 gives a summary of the traffic volume recorded during the 2 years of the study as overall average number of vehicles per day. Both roads No.2 and 3 were very lightly travelled with increased traffic densities on roads No.1 and 4. The increased traffic on road No.1 during 78 compared to 77 was consistent over the period of observation. As a result of the low traffic volumes on all test roads, automotive exhausts could be disregarded as a measurable source of lead contamination in the roadside environment. Therefore, any concentrations of lead determined above the natural background values would be attributable to external sources of contamination, such as the materials used as dust suppressants.

Rainfall during the period May to November 1978 was near average with respect to total rainfall, however June and July recorded below average rainfall, while August and September had above average rainfall with September showing a total precipitation of 133mm for 2 times the monthly average.

The waste oil used for the 1978 study had a specific gravity of 0.923 and an oil content of approximately 70% by weight measured as HEM. The concentrations of lead and zinc were respectively 4.34 g/l and 1.25 g/l. Cadmium was present at 5.8 mg/l. Copper was present at 31.1 mg/l, chromium at 12.5 mg/l and arsenic at 29.5 mg/l.

3. DISCUSSION OF OBSERVATIONS AND RESULTS, (cont'd):

The GLC analysis showed that any PCB present in the waste oil would be below the detection limit of this method (5 mg/l).

The calcium chloride used for dust control in 1978 had a specific gravity of 1.346 and a chloride content of 315 g/l, corresponding to a CaCl_2 content of 36.5% by weight. The liquid CaCl_2 had a trace of oil measuring 8 mg/l as HEM.

The revised sampling programme used during 1978 for the road bed and shoulder soil provided 5 grab samples per test section for each composite sample at a frequency of once every 2 weeks. Inspite of a remaining fluctuation of data, a trend could be established providing a basis for data analysis and possible conclusions.

The data in Table 2 indicate the variation of HEM content in road bed samples during the 1978 sampling period. The May samples were taken before application of the waste oil and showed the residual HEM in road 1 at 7.5 mg/g and 0.02 mg/g in road 4, as the oil section of this road had been regraded in the early spring. The data show a general trend toward the pre-application level in the case of road 1. It is noted that road 4 did not decrease to the pre-application value, but stayed at a higher value than road 1. This pattern may be similar to that shown by road 3, where without further treatment in 1978 the road bed showed a continuous decrease from 7 mg/g in June to 1.1 by March 1979.

The lead present in the waste oil appeared to behave quite differently from the oil itself once exposed to conditions in the road bed, as shown by the data in Table 3. The data suggest a more or less random fluctuation rather than any identifiable trend and no gradual decrease of the lead concentrations. Apparently lead was retained in the road bed aggregate.

As shown in Table 4 the chlorides in the road bed increased as a result of the initial application on both test roads, followed by a gradual decline specially during the month of September with its above average rainfall. The disappearance of the chloride would be under influence of the rain water effecting the leaching of chlorides from the road bed aggregate.

3. DISCUSSION OF OBSERVATIONS AND RESULTS, (cont'd):

The data thus indicated that both with oil treatment and with calcium chloride the materials added to the road bed for dust suppression were lost to the environment during the period of observation. Sampling of run-off water from the road bed as it entered the road shoulder or the roadside ditches gave confirmation of the transport route for these materials leaving the road bed as shown in Table 5. In the run-off water from the chloride treated sections chloride concentrations as high as 260 mg/l were observed. From the oil treated sections HEM concentrations to 220 and 350 mg/l were found. The very low concentrations of lead agree with the concept that lead is retained in the road bed since the ratio HEM:lead in the run-off water was in the order of 4,000:1 compared to the waste oil sample showing a ratio of approximately 150:1.

In addition to the run-off water samples a number of miscellaneous samples have been collected and analyzed, to obtain analytical evidence of the presence of either oil or calcium chloride in areas away from the road bed. Table 6 presents a brief summary of this information. The stream sample was taken downstream of road 1 in a stagnant area just upstream from where a tributary joined the stream. The 90 mg/l HEM content provides confirmation of the observed oily scum accumulated in that location. The other samples presented in Table 6 represent areas of visible contamination with waste oil and the results at least confirm the presence of oily material. It is interesting though that the actual numbers were equal to or lower than the road bed oil concentrations, except for one sample.

A totally separate study could be made of the subject of dust generation, sample collection and chemical analysis in relation to processes occurring in the road bed under influence of traffic usage. Particulates in automotive exhausts would need to be considered as well.

The data in Table 7 show that the high volume air samplers collected dusts with somewhat similar chemical characteristics, although the sections of road were typically different, oil treated vs CaCl_2 treated. It is noted that both the HEM and the lead contents of both types of dust are very much higher than recorded for the road bed samples.

3. DISCUSSION OF OBSERVATIONS AND RESULTS, (cont'd):

For comparison Table 7 also presents chemical characteristics of dust samples obtained from the dustfall collectors, specifically with respect to the lead content. Although the measured lead concentrations in the dust samples are significantly lower than those obtained for the high volume air samplers, the dust lead content is still higher than the corresponding values found in the road bed samples.

Some clarification of the problem may be obtained from a study of the results in Table 8, which show the penetration of materials into the road bed. The highest concentrations of all three parameters were found in the upper 2.5 cm layer. This feature applied particularly to the lead but also to the HEM. It would seem that the lead remains in the upper layer of road bed surface material, and that this layer produces most of the dust. It was reassuring to find that the average concentrations of constituent for the upper 10 cm layer based on the data in Table 8 compared well with the road bed samples taken during the same period represented by each of the depth profiles.

4. SUMMARY:

From the data collected during the study programme, some of which we have reviewed in this presentation, we have prepared the following summary.

- 4.1 Any PCB's present in the waste oil used in 1978 were below the 5 ppm detection limit of the GLC.
- 4.2 The observed loss of waste oil from the 1978 test roads was approximately equal to the quantity of waste oil applied in 1978.
- 4.3 The prime transfer route was via the run-off water during rainfall, which resulted in some accumulation in the adjacent road shoulders.
- 4.4 After a single application of waste oil for dust control, oil losses from the road bed continued into the second year, with a residual oil content still above the background level. The dust control effectiveness was lost within 6 months after the application.

4. SUMMARY, (cont'd):

- 4.5 Samples of run-off water showed oil concentrations consistently above the MOE objectives of 15 mg/l HEM for industrial waste discharges to receiving streams.
- 4.6 Oil-coated fines were found in adjacent shoulders and fields, as temporary storage areas for continued transport from there with the run-off water.
- 4.7 Lead compounds present in the waste oil seemed to be retained in the road bed aggregate and showed a very slow rate of loss compared to the oily materials.
- 4.8 Dust analysis showed higher concentrations of HEM and lead per gram of dust than in the road bed. Dust collected with the high volume air samplers showed similar high concentrations of materials for both the oil and CaCl_2 sections.
- 4.9 The lead content of settleable dust was consistently higher for the oil treated section than for the control or CaCl_2 sections, likely as a result of the oil treatment.
- 4.10 Loss of chlorides from the CaCl_2 treated roads was effected mainly by rainfall and run-off and subsequent discharge to the receiving stream. Most of the applied chloride was lost from the test roads during the first 5 months after application.
- 4.11 Analysis of settleable dust data indicated that dust control with waste oil was equally effective as that using CaCl_2 . Treatment with CaCl_2 allowed the road surface to retain its dust control characteristics even after regrading.
- 4.12 We have found that materials for dust control are lost from the road bed under influence of rainfall and run-off, independent of whether the material is soluble in water. Entry into the local road environment will follow the local drainage pattern, perhaps with intermediate storage areas. Eventual discharge into nearby receiving streams or lakes can be expected.

4. SUMMARY, (cont'd):

4.13 The scope of this study programme did not permit an assessment of the environmental effects, due to the short period of observation and the low levels of material transferred into the roadside environment. Complex physical chemical reactions must be taken into consideration, covering the exposure of soil, sand, gravel and vegetable matter to inputs of organic and/or inorganic chemicals, when attempts are made to predict the transport of materials from the road bed into the roadside environment and their possible effects on that environment.

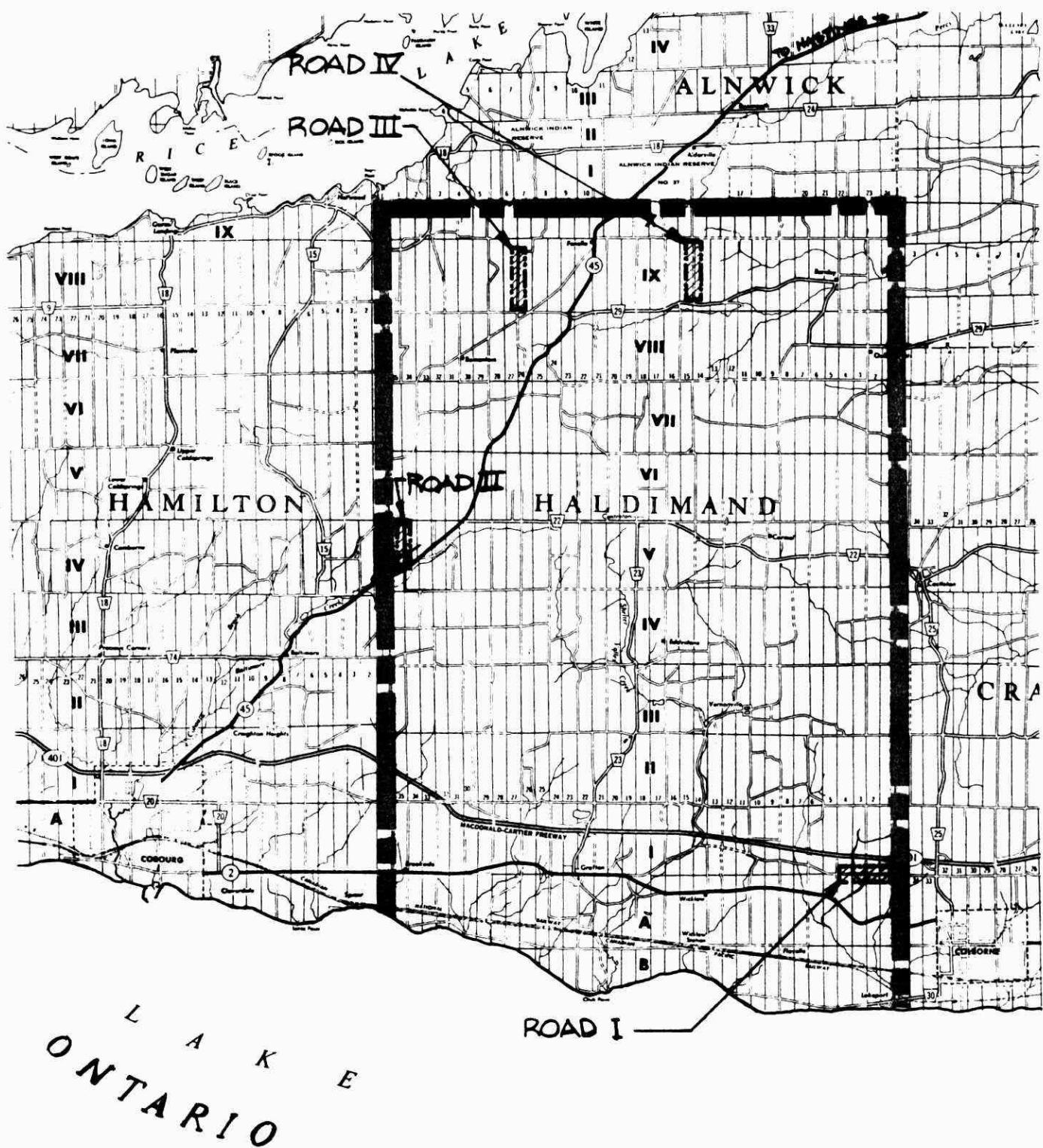


FIGURE NO. I

TABLE 1

TRAFFIC VOLUME
VEHICLES PER DAY

ROAD	1	2	3	4
1977	79	15	13	70
1978	112	-	-	72

TABLE 2

OIL IN ROAD BED

mg HEM/g

DATE	Road 1	Road 4	Road 3
1978			
May	7.5	0.02	-
June	19.5	14.0	7.0
July	14.4	10.5	6.7
Sept.	10.4	7.5	3.2
Oct.	9.4	6.5	3.4
March, 1979	7.4	8.3	1.1
Control	0.1	0.44	0.05

TABLE 3
LEAD IN ROAD BED
mg/g

DATE	Road 1	Road 4
1978		
May	0.10	0.03
June	0.14	0.13
July	0.12	0.10
September	0.09	0.10
October	0.11	0.09
March, 1979	0.15	0.11
Control	0.03	0.05

TABLE 4
CHLORIDE IN ROAD BED
mg/g

DATE	Road 1	Road 4
1978		
May	0.02	0.01
June	2.6	0.8
July	2.9	2.3
August	2.1	1.4
September	0.2	0.5
November	0.1	0.03
Control	0.09	0.04

TABLE 5
RUN-OFF WATER
mg/l

	CaCl ₂	OIL	
Road 1; '77	150 C1	-	-
Road 1; '78	24 C1	220 HEM	0.06 Pb
Road 4; '78	-	150 HEM	0.02 Pb
Road 2; '77	260 C1	350 HEM	-

TABLE 6
MISCELLANEOUS SAMPLES
OIL SECTION

1978	HEM	
Road 1 Stream	90 mg/l	0.1 mg/l Pb.
Road 4 Shoulder fines	6.3 mg/g	
Road 4 Run-off fines	0.72 mg/g	
Road 4 Shoulder soil	2.15 mg/g	
Road 4 Shoulder soil	45.0 mg/g	

TABLE 7
DUST CHARACTERISTICS

1. High Volume air Samplers				
		Average	Maximum	Minimum
1.1	Oil Section			
	dust mg/h	9.8	33.6	2.2
	HEM mg/g	96	479	8.8
	Pb mg/g	2.8	4.53	0.49
1.2	CaCl ₂ Section			
	dust mg/h	13.7	50.6	2.6
	HEM mg/g	55	193	4.2
	Pb mg/g	2.0	3.55	0.19
	Cl mg/g	6.3	10.6	0.85
2.	Dust Collectors			
2.1	Oil Section			
	dust g/m ² /day	0.14	0.18	0.10
	Pb mg/g	0.53	0.71	0.35
2.2	CaCl ₂ Section			
	dust g/m ² /day	0.25	0.29	0.20
	Pb mg/g	0.07	0.09	0.04
2.3	Control			
	dust g/m ² /day	0.38	0.45	0.22
	Pb mg/g	0.15	0.17	0.12
3	Road Bed oil	0.09 mg/g Pb		
	CaCl ₂	0.03 mg/g Pb		
	Control	0.03 mg/g Pb		

TABLE 8
PENETRATION INTO ROAD BED, mg/g

Depth cm	June		Oil Section		October		CaCl ₂ June C1	Section October C1
	HEM	Pb	HEM	Pb	HEM	Pb		
0 - 2.5	29.9	0.25			14.3	0.17	4.9	0.7
2.5 - 5	9.0	0.06			9.4	0.09	3.2	0.5
5 - 10	8.8	0.07			1.6	0.05	0.45	0.5
10 - 15	6.8	0.06			1.6	0.13	0.22	0.6
15 - 20	4.1	0.08			1.3	0.07	0.11	0.3
20 - 25	1.3	0.03			0.57	0.04	0.04	0.3
25 - 30	0.12	0.02			0.12	0.02	0.02	0.1

THE EFFECTS OF ROAD OILING ON
PCB ACCUMULATION IN AQUATIC LIFE

LTS 80-5

by

K. Suns, C. Curry, D. Wilkins and G. Crawford
Ontario Ministry of the Environment
Box 213, Rexdale, Ontario
September, 1980

TABLE OF CONTENTS

	page
PREFACE.....	i
SUMMARY.....	ii
INTRODUCTION.....	1
METHODS	
Fish Residue Investigations.....	1
Caged Freshwater Clams - Dickie Lake.....	4
Sediments.....	6
RESULTS AND DISCUSSIONS	
Fish Residues.....	8
Caged Freshwater Clams.....	8
Sediments.....	10
CONCLUSIONS AND RECOMMENDATIONS.....	11
LITERATURE CITED.....	12
ACKNOWLEDGEMENTS.....	13

PREFACE

During the past few years there has been growing concern over the increasing numbers of fish contaminants in Ontario lakes and rivers. Many contaminants reach concentrations in fish which pose a risk for human consumption, while the health of the fish themselves does not appear to be affected. Consequently, human consumption of fish from some waters must be controlled because of their content of materials such as mercury or PCB's.

Effective major fish analyses programs have been directed toward the sport fish populations in order to develop appropriate human consumption guidelines. However, due to ageing difficulties and their wide-ranging life-style contaminant residue data of adult fish do not shed much light on some fundamental questions regarding contaminant control, such as location of sources, trends with time and mechanisms of uptake.

To augment the adult sport fish surveys, the Toxicity Unit began in 1975 to conduct contaminant surveys of young fish. The program concentrates on young-of-the-year, or yearlings of a variety of species. Such fish can be easily aged and they represent current contaminant uptake conditions. The young fish have a limited range, so their contaminant uptake represents also a narrow range of space conditions. While the results may not be relevant to human consumption of sport fish from the same waters, they provide good scientific data for determining contaminant uptake as a function of time and geographic location.

This concept is being applied to investigate a number of areas of concern in the Province. The young fish surveys are supported by a variety of chemical and biological collections to suit the specific purpose of the investigation.

This report deals with the practice of waste oil use for dust control and its effect on PCB uptake in yellow perch and freshwater clams in the receiving waters.

Summary

PCB residue concentrations were determined in yearling yellow perch from twelve Muskoka lakes to evaluate the effects of road oiling on PCB uptake. Fish residue analyses have shown that PCB's were significantly ($P < 0.05$) elevated in lakes that were affected by the run-off from waste oil applications. Furthermore, 71% of all the fish samples analyzed from lakes affected by road oiling exceeded the PCB guideline for wildlife protection (I.J.C. 1977), while PCB residues in non-affected lakes were considerably lower.

A study using freshwater clams in Dickie Lake demonstrated that PCB uptake in the nearshore biota was affected by drainage characteristics and the proximity of waste oil application sites to the receiving waters. Although the PCB residue concentrations in waste oils applied were considerably below the Ontario Pollution Prevention Guideline of 25 ppm, a significant ($p < 0.05$) uptake of PCB's was observed in caged freshwater clams.

Stream sediment analyses showed that the highest PCB concentrations existed immediately below the oiled road in the stream bed.

INTRODUCTION

Although the practice of using contaminated waste oils for dust control is well established, little is known of the environmental impact associated with it. A report prepared for the Ontario Ministry of the Environment and Ministry of Transportation and Communications on the Effects of Waste Oil as a Road Dust Suppressant (L.S. Love & Associates 1978) concludes that runoff is the major route for transfer of waste oils from the road surfaces. Therefore, it can be expected that any contaminants in waste oils will eventually be discharged to surface waters. EPA's Water Quality Research Laboratory in Edison, N.J. (Waste Oil Fact Sheet) has also demonstrated that about 99% of the oils applied to rural road surfaces left the surfaces either as dust particles or in water runoff. While the waste oil movements were documented by both studies, the effects on the aquatic life in receiving waters have not been evaluated.

The presence of PCB residues in waste oils and the repetitive nature of road oiling in Ontario has raised questions regarding the possibility of PCB accumulations in the aquatic biota. The concerns over present road oiling practices have been documented by L.S. Love and Associates (1978), and the study concludes that the potential for receiving water contamination exists.

The present study was initiated following observations of anomalous PCB residue distributions in yearling yellow perch from Muskoka lakes.

METHODS

Fish Residue Investigations

In order to explain elevated PCB residues in fish from some Muskoka lakes used only for recreational purposes, PCB residue concentrations in fish from areas with known road oiling activities were compared with fish residues from lakes where oiling was not practiced. Twelve Precambrian lakes were used for the survey and were classified either as affected or not affected by waste oil applications (Fig. 1). Table 1. The criterion used for lake separation was the presence or absence of road oiling in lake drainage basins, as shown by township road oiling records. No attempt was made to quantify waste oil applications

TABLE 1.
COMPARISONS OF PCB RESIDUES IN YEARLING YELLOW PERCH FROM
OILED AND NOT-OILED WATERSHEDS

Locality	N*	Fish Size T.L. (mm)	Fish Weight (g)	% Fat	PCB Concentration (ng/g \pm S.D.)
<u>Not Oiled</u>					
Cranberry Lake	7	106 \pm 1	12.9 \pm 3.5	5.2 \pm 1.4	38 \pm 16
Bigwind Lake	6	74 \pm 6	3.6 \pm 1.0	2.8 \pm 0.4	10 \pm 19
Chub Lake	9	82 \pm 6	5.2 \pm 1.3	2.4 \pm 0.4	Trace
Leonard Lake	10	75 \pm 3	3.9 \pm 0.6	2.4 \pm 0.9	Trace
Nelson Lake	10	82 \pm 3	4.5 \pm 1.4	2.1 \pm 0.3	11 \pm 12
<u>Oiled</u>					
Duck Lake	9	97 \pm 3	8.2 \pm 1.0	2.4 \pm 0.5	79 \pm 14
Healey Lake	10	83 \pm 2	5.5 \pm 0.5	5.0 \pm 0.2	89 \pm 45
Harp Lake	10	65 \pm 3	2.4 \pm 0.3	1.2 \pm 0.1	101 \pm 53
Fawn Lake	10	88 \pm 4	6.3 \pm 1.0	3.9 \pm 0.4	146 \pm 56
Little Clear Lake	10	70 \pm 3	3.2 \pm 0.5	3.3 \pm 0.4	172 \pm 67
Heeney Lake	10	79 \pm 2	4.2 \pm 0.3	3.0 \pm 0.4	256 \pm 84
Dickie Lake	10	67 \pm 3	2.6 \pm 0.4	3.3 \pm 0.3	307 \pm 70

*Each sample is a composite of 8 fish.

Detection Limit

10 ng/g

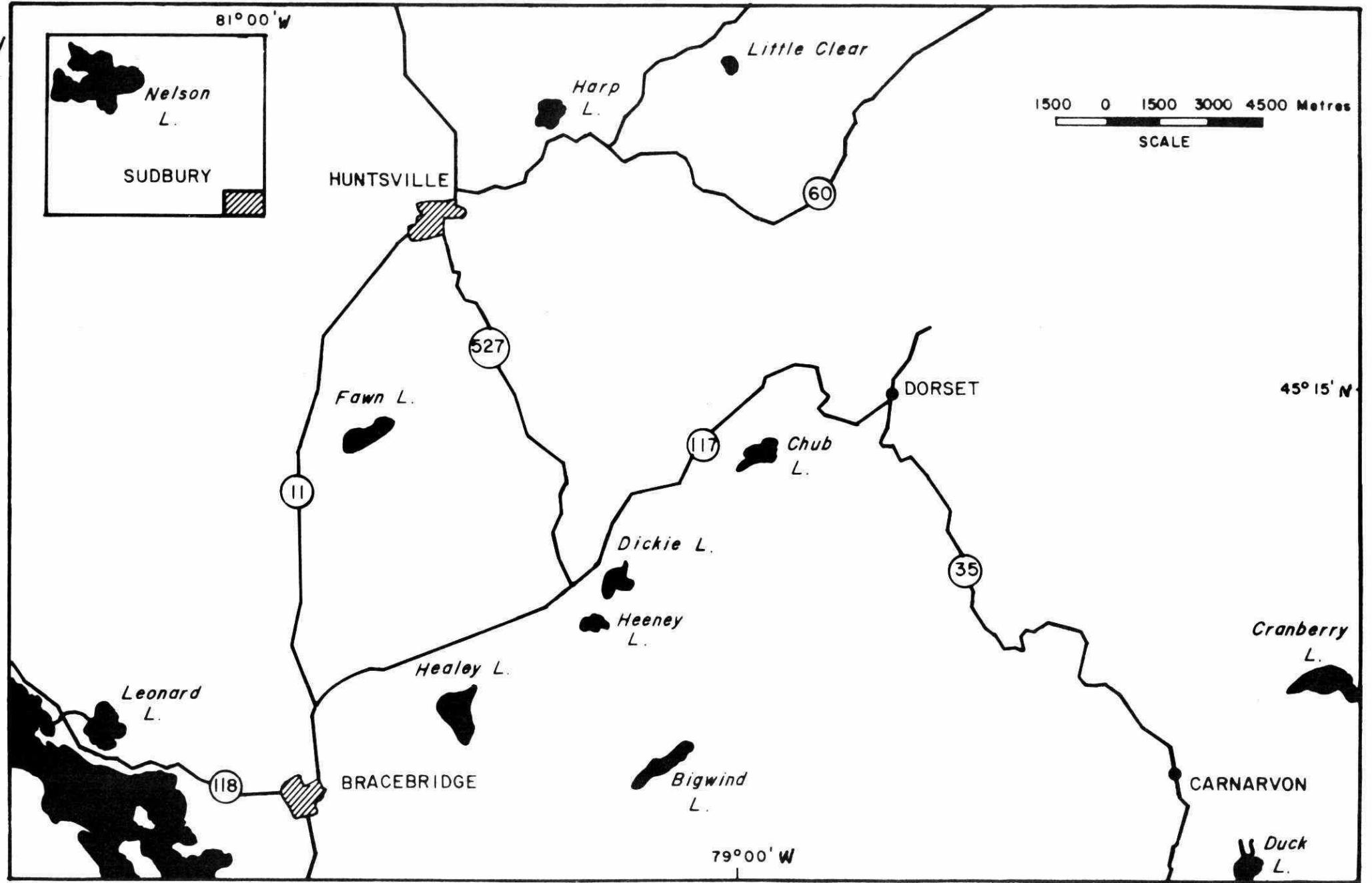


FIGURE 1 : STUDY AREA, MUSKOKA LAKES

in individual drainage basins.

Samples of young yellow perch (*Perca flavescens*) were collected for body-burden determinations. Individual fish were measured, weighed and scale samples taken from representative size groups. Fish ageing confirmed that all samples belonged to the yearling (1+) age class. The selection of a specific age class provided residue data that were spatially comparable. Composite samples of 8 fish each per site were wrapped in hexane-washed aluminum foil and frozen in the field. PCB residues were determined for composite whole fish samples, and analytical results were reported on a wet-weight basis. Student's "t" tests were done to compare differences between means. All analyses were done at the Ministry of the Environment Pesticides Laboratory at Rexdale by gas-chromatography methods. Detailed methodologies are available from the Handbook of Analytical Methods for Environmental Samples, Laboratory Services Branch, Ontario Ministry of the Environment.

DICKIE LAKE STUDY

Caged Freshwater Clams

In addition to the fish residue investigations, a study was undertaken at Dickie Lake in 1979 to assess site-specific effects of road oiling. Caged freshwater clams (*Elliptio complanata*) were used to evaluate PCB uptake at three nearshore sites in the lake (Fig. 2).

Live freshwater clams were collected from Balsam Lake in Bexley & Fenelon Township and transferred to Dickie Lake. PCB concentrations in Balsam Lake clams were typically at trace levels, and therefore may be considered representative of background conditions. Each clam was individually measured and weighed, and 15 clams were placed in each wire cage (22 x 21 x 15 cm). Caged clams were placed on lake sediments near Dickie Lake inflows #8, #9 and the lake outflow at locations C1, C2 and C3 (Fig. 2). Clams were located at site C1 adjacent to the oiled road on two occasions, first (June 5-19) prior to the season's oil application and secondly (June 19-July 10) after oiling. Road oiling was carried out on the 18th of June. The initial exposure was intended to evaluate PCB uptake from previous season's residuals.

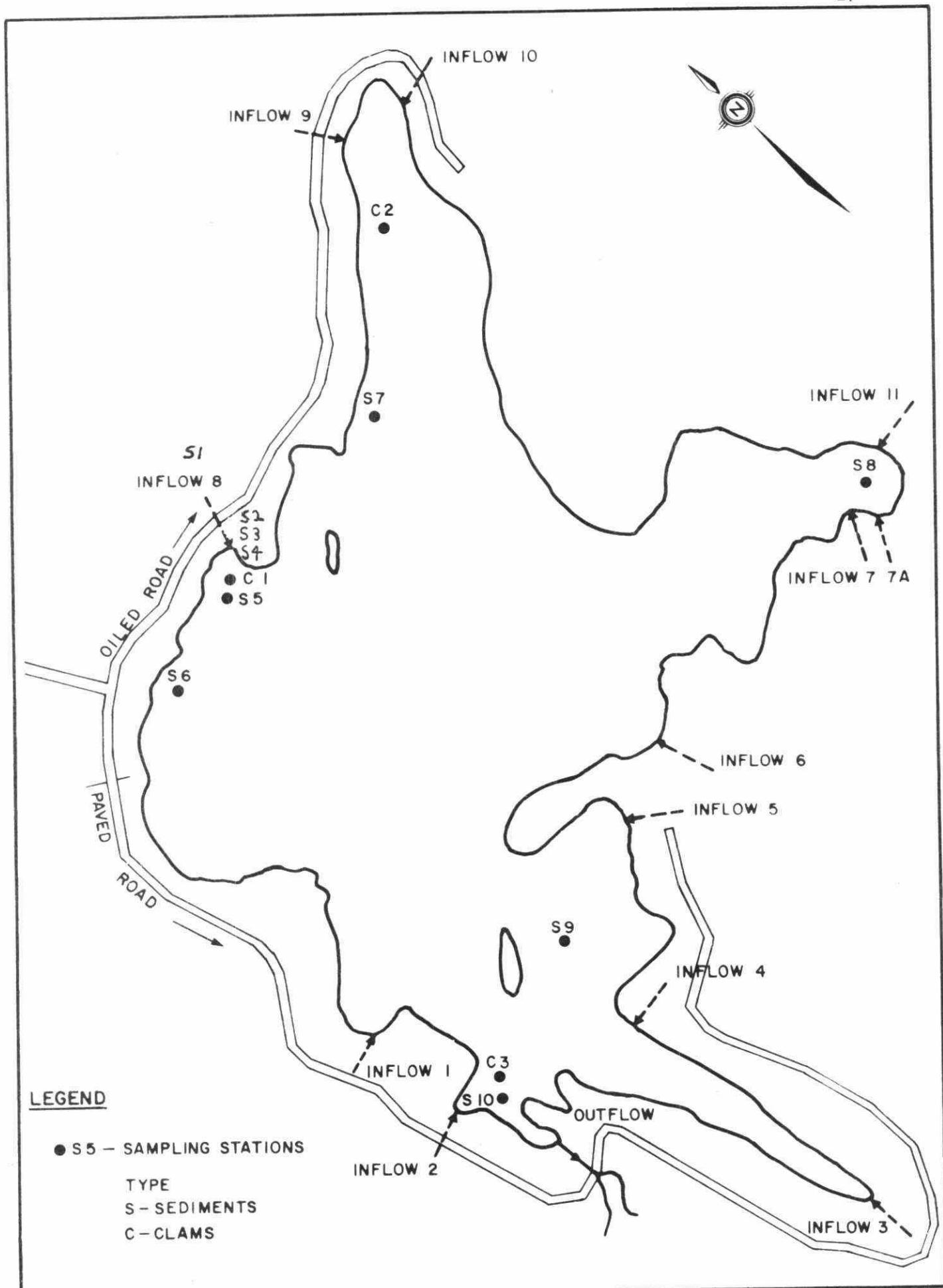


FIGURE 2 : DICKIE LAKE SITES

PCB's and fat content determinations were done by azeotropic distillation using benzene. Details of the analytical methodologies employed are available from the Handbook of Analytical Methods for Environmental Samples, Laboratory Services Branch, Ontario Ministry of the Environment.

Sediments

Sediment samples were collected at ten sites for PCB analyses (Fig. 2). Most samples were obtained with a 5 cm diameter push-rod corer of Water Resources Branch design, but Station S9 was sampled with a 23 x 23 cm ponar dredge. The control site (S1) was located about 50 meters upstream of the perimeter road on inflow #8 in a marshy area with very organic soils. Downstream from the road and around the perimeter of the lake the sediments were predominantly sandy with varying fractions of organic detritus. Some construction activity just downstream from the road (installation of a weir on #8 inflow) may have induced recent siltation in the stream, but visual observations revealed only minor silt deposits.

Station S9 in a deep sheltered basin was the only lake station sampled which represented a true depositional environment. Any contaminants in the nearshore sands would be indicative of fairly recent inputs that would ultimately be resuspended and transported to a depositional area.

Core samples were of varying lengths due to variations in sediment types and the inability of the push-rod corer to penetrate through roots, stones and clam shells. Cores were extruded directly into wide mouth glass jars, one sample for the top half of the core and one sample for the bottom half. Details of core lengths are given in Table 3.

In addition to PCB's, the sediments were analyzed for mercury, copper, zinc, lead, aluminum and nickel. All analyses were done at the Ontario Ministry of the Environment Laboratories in Rexdale.

TABLE 3.

PCB RESIDUES IN DICKIE LAKE

SEDIMENTS - 1979

Station No.	Depth Interval	Description	PCBs (µg/kg)
Station 1 Upstream Control	Surface to 10 cm 10 cm to 20 cm	Highly Organic Black Silt	ND ND
Station 2 Roadside	Surface to 5 cm	Brown Organics Sand with Roots	1000
Station 3 Stream half way to lake	Surface to 10 cm 10 cm to 15 cm Scoop of Surface 2 cm	Coarse Sand over Organic Silt Loose Organic Silt	ND 200 240
Station 4 Stream Mouth	Surface to 9 cm 0 cm to 20 cm	Coarse Sand & Org. Med. Sand & Org.	ND 20
Station 5	Surface to 12 cm 12 cm to 24 cm	Medium Sand & Org. over Fine Sand	20 ND
Station 6	Surface to 10 cm 25 cm to 35 cm	Fine Sand Some Organic Debris Fine to Coarse Sand	ND ND
Station 7	Surface to 6 cm 6 to 16 cm	Vegetation over Sand with Pyrites Sand	ND ND
Station 8	Surface to 13 cm 13 to 26 cm	Sand with Trace Org. Fine Sand	ND ND
Station 9	Ponar Surface to 5 cm	Organic Silt Coze	150
Station 10 Lake Outlet	Surface to 8 cm 8 to 15 cm	Vegetation over sand Coarse Sand and Organic Debris	ND ND
Detection Limit			10

N.D. - Non detectable

RESULTS AND DISCUSSIONS

Fish Residues

Mean PCB residue concentrations in yearling yellow perch from lakes where road oiling occurred, ranged from 79 - 307 ng/g; whereas fish residues from lakes where oils were not used on roads as dust suppressant ranged from 3-38 ng/g (Table 1). The respective means for each group were 166 ± 100 ng/g and 12 ± 15 ng/g ($p < 0.05$). The typical composition of PCB residues in fish were Aroclors 1254 and 1260 in a 4:1 ratio.

Since metabolic rates, exposure times and contaminant concentrations govern contaminant uptake in fishes (de Freitas 1976; Nebeker 1975; Kelso and Frank 1974), a degree of uniformity of fish sizes, ages and lipid contents is necessary for valid spatial contaminant level comparisons. The use of yearling yellow perch as a biological integrator satisfies these criteria. The collection of a specific age class has ensured a similar exposure period, and the absence of statistically significant ($p > 0.05$) correlations between PCB residues in fish, their sizes and lipid contents suggest that PCB residue differences cannot be attributed to differences in metabolic activity. It may be concluded, therefore, that the major differences in PCB residue concentrations in fish were related to PCB availability.

The I.J.C. (1977) guideline (100 ng/g) for PCB's in fish, established for the protection of wildlife and fish-eating birds were exceeded in 71% of the lakes affected by road oiling, whereas fish residues in the non-affected lakes remained well below this guideline limit. PCB concentrations in yearling yellow perch from these recreational lakes were of the same order of magnitude as residues found in lakes with known industrial or municipal PCB inputs, such as Lake Simcoe and Lake Muskoka (Suns *et al.* 1978), or several industrialized sites on Lake Ontario (Trenton - 346 ng/g; Moira River - 308 ng/g; Cornwall - 138 ng/g).

While the fish residue data from this survey demonstrate that PCB inputs from waste oil applications have significantly influenced PCB residue concentrations in nearshore fishes of the receiving waters, the degree and extent of PCB accumulation in adult sportfish remains undetermined.

TABLE 2.

PCB UPTAKE RESULTS IN CAGED FRESHWATER CLAMS

DICKIE LAKE - 1979

	Stn. No.	N	Clam Size (mm)	Clam Weight (g)	% Fat	PCB Concentration (ng/g)
Pre-Oiling	C1	5	73 ± 1	6.8 ± 0.7	1.0 ± 0.2	N.D.
Post-Oiling	C1	5	70 ± 1	6.6 ± 1.0	0.8 ± 0.2	19 ± 4
	C2	5	74 ± 1	7.9 ± 0.8	0.9 ± 0.2	15 ± 11
	C3	5	74 ± 4	7.3 ± 1.2	1.0 ± 0.3	Trace

N.D. - Non detectable

Detection Limit 10 ng/g

Caged Freshwater Clams

No PCB residue accumulations were detected in freshwater clams after a 14 day exposure at Dickie Lake inflow #8 (C1) prior to the 1979 road oiling activities (Table 2). Lack of PCB residue accumulations from previous season's oiling activities indicates that PCB inputs can be effectively reduced if alternative dust-control practices were implemented. Freshwater clam evaluation studies have shown that a 14 day exposure period is long enough to demonstrate a measurable PCB uptake (Curry 1977). Following the road oiling on June 18, and after a 21 day exposure, significantly higher ($p < 0.5$) PCB accumulations were detected in caged clams at site C1 (19 ng/g) and site C2 (15 ng/g), compared to site C3 (2 ng/g) at the lake outflow. Both sites C1 and C2 were exposed to runoff from waste oil applications, whereas site C3 was not. These results suggest that PCB residue runoff from oiled road surfaces affects PCB accumulations in the nearshore biota. The effects are site-specific, and it appears that PCB residuals from prior season's applications did not affect residue accumulations significantly. It is interesting to note that soil sample analyses from Dickie Lake road showed PCB concentrations ranging from 12.6 ppm - 20.0 ppm in the oils used in 1979. These levels were below the Pollution Prevention Guidelines (1978) level of 25.0 ppm, yet a significant uptake of PCB's by the freshwater clams was observed in nearshore waters.

Sediments

No PCB's were detected in the sediments at the upstream control site (S1), while elevated PCB concentrations were found downstream of the road, with the highest concentrations closest to the oiled road (Stn. S2), as shown in Table 3. The PCB residues found resembled a one-to-one mixture of Aroclor 1254 and 1260. PCB residues were still twice the detection limit at the stream mouth (S4) and about 60 metres down the shoreline (S5), in spite of the predominantly sandy nature of the sediments. No PCB's were detected at the other sandy nearshore stations including the bay near the lake outflow (S10). PCB residues from the deep basin sediments of the lake (S9) at 150 $\mu\text{g}/\text{kg}$ showed convincingly that PCB's accumulate in the lake in association with the

fine grain-sized material. In comparison the mean PCB concentration for Lake Ontario sediments, a lake with known PCB inputs, has been reported to be 57 $\mu\text{g}/\text{kg}$ (Frank et al. 1979), while PCB residues for Lake Huron sediments ranged from 9-33 $\mu\text{g}/\text{kg}$ (PLUARG 1978).

In order to determine the potential metals inputs from waste oil applications, metals residues from Dickie Lake sediments were compared to metals data from lakes not exposed to waste oil inputs. It was found that lead (<3-130 $\mu\text{g}/\text{g}$), copper (<3-24 $\mu\text{g}/\text{g}$), zinc (5-170 $\mu\text{g}/\text{g}$), nickel (<3-10 $\mu\text{g}/\text{g}$), mercury (<.01-.52 $\mu\text{g}/\text{g}$) and aluminum (1-10 mg/g) concentrations in Dickie Lake sediments were not outside the typical metals ranges found in other Muskoka lakes (P. Dillon, personal comm.). Therefore it may be concluded that waste oils were not a major contributor of metals in the Dickie Lake watershed.

CONCLUSIONS AND RECOMMENDATIONS

PCB residues in juvenile yellow perch were found to be significantly elevated in watersheds where waste oils were used for dust control, as compared to lakes where road oiling was not practised. Fish residue concentrations in 71% of all fish samples analyzed from lakes affected by road oiling exceeded the PCB guideline established for the protection of wildlife and fish-eating birds.

PCB uptake results from the caged clam study in Dickie Lake showed that PCB accumulations in nearshore biota were affected by drainage characteristics and the proximity of oiled roads to receiving waters. The caged clam study results also suggest that PCB residuals from prior season's waste oil applications do not affect residue accumulations significantly.

It should be noted that significant PCB accumulations in the near-shore biota resulted from waste oil applications that contained PCB residues below the existing Pollution Prevention Guideline of 25 ppm. Therefore the PCB content in waste oils should be reduced in cases where the receiving waters are affected by run-off from waste oil applications.

While this study has demonstrated that waste oil applications do enhance PCB uptake in the biota of receiving waters, the impact on the sport fishery remains unknown. A PCB residue survey of adult sportfish in selected Muskoka lakes is planned for the 1980 field season.

REFERENCES

CURRY, C. 1977-78. The freshwater clam (Elliptio complanata), a practical tool for monitoring water quality. *Water Pollution Research in Canada*. Vol. 13:45-51.

deFREITAS, A.S.W. A model for pollutant accumulation by fish. Ottawa River Project. Report No. 3, January 1976. University of Ottawa - National Research Council of Canada.

FRANK, R., R.L. THOMAS, M. HOLDRENET, A.L. KEMP and H.E. BRAUN. 1979. Organochlorine insecticides and PCB in surficial sediments and sediment cores. *Journal for Great Lakes Research*. Vol. 5, No. 1.

I.J.C. 1977. New and Revised Great Lakes Water Quality Objectives. Vol. 2, October 1977.

LOVE, L.S. & ASSOCIATES CANADA LIMITED. "Report on the Environmental Effects of Waste Oil as a Road Dust Suppressant" - for the Ontario Ministry of the Environment, Pollution Control Branch, Toronto Report #595, March 1978.

NEBEKER, A.V. 1976. Summary of recent information regarding effects of PCB's on freshwater organisms. *Proceedings of National Conference on Polychlorinated Biphenyls*. 1976. E.P.A. Office of Toxic Substances.

PLUARG, 1978. Environmental Management strategy for the Great Lakes System. International Joint Commission 1978. pp.39-40.

POLLUTION PREVENTION AND WASTE MANAGEMENT GUIDELINES FOR POLYCHLORINATED BIPHENYLS. Ontario Ministry of the Environment, Waste Management Branch. September, 1978.

SUNS, K., M. JACKSON, G.A. REES and R. McVICARS. 1978. The use of yearling yellow perch as indicators of organic chemicals and mercury contamination in selected Ontario lakes. Ontario Ministry of the Environment. LTS 79-3. 1978.

"WASTE OIL FACT SHEET" prepared by Industrial Analysis Office, Energy Conservation and Environment, Federal Energy Administration, Washington, D.C. 20461, June 1976. (ref. for the EPA's Water Quality Research Laboratory in Edison, N.J.).

Acknowledgements

We thank D. Andrews and F. Hedley for their assistance with sample collections.

We are especially indebted to A.F. Johnson for valuable ideas and the necessary background for road oiling activities.

Dr. T. G. Brydges and G.R. Craig supplied valuable comments and criticisms on the manuscript.

WASTE OIL UTILIZATION

1975

- MINISTRY OF ENERGY FORMED
- PROJECT DEVELOPED TO STUDY WASTE OIL UTILIZATION
- FOLLOWED FROM FEDERAL/PROVINCIAL STUDY ON BURNING OF WASTE CRANKCASE OIL IN CEMENT KILNS

TASK FORCE OR COMMITTEE FORMED

MIN. OF ENERGY
MIN. OF TRANS. & COMM.
MIN. OF IND. & TOURISM
MIN. OF ENVIRONMENT

OBJECTIVE

TO REVIEW WASTE OIL SITUATION AND
MAKE RECOMMENDATIONS ON POLICIES FOR
WASTE OIL UTILIZATION.

WASTE OIL RECYCLING STUDY

1975 TEKNEKRON INC. RETAINED TO STUDY WASTE OIL RECYCLING POTENTIAL

OBJECTIVES

- COMPILE DATA ON AMOUNTS OF WASTE OIL GENERATED
- REVIEW REREFINING PROCESSES
 - COST
 - PRODUCT ACCEPTABILITY,
- ENVIRONMENTAL IMPACTS OF REREFINING PROCESSES
- REVIEW ALTERNATIVE TECHNOLOGIES FOR UTILIZATION OR DISPOSAL OF WASTE OIL.

REPORT COMPLETED IN MARCH 1976

FINDINGS OF TEKNERRON REPORT

1) WASTE OIL VOLUMES (LUBRICATING OIL)

10 MILLION GALLONS IN ONTARIO

87 MILLION GALLONS PER YEAR SOLD

55 MILLION GALLONS PER YEAR CONSUMED (ESTIMATE)

22 MILLION GALLONS PER YEAR UNACCOUNTED

2) CURRENT DISPOSAL OF WASTE OIL

- ROAD OILING - 6-7 MIL

- BURNING AS FUEL - 2-3 MIL

- REREFINING (BRESLUBE) - 1.0-1.5 MIL

3) REREFINING PROCESS

1) DEHYDRATION/CLAY (RECOMMENDED)

2) DISTILLATION/CLAY

3) DISTILLATION/HYDROTREATMENT

4) ACID/CLAY

5) EXTRACTION/ACID/CLAY

RANKED AS ABOVE ON FOLLOWING CRITERIA:

- ENVIRONMENTAL - 20%

- QUALITY OF PRODUCT - 20%

- PRODUCT RANGE - 5%

- FEED STOCK AVAILABILITY AND MARKET ASSESSMENT - 15%

- ECONOMICS - 40%

EACH PROCESS FOUND TO BE PRACTICABLE ALTHOUGH ACID/CLAY
FOUND TO BE MARGINABLE.

FINDINGS OF TEKNERRON REPORT (CONT'D)

- 4) ALTERNATIVE DISPOSAL OR USE TECHNOLOGIES
 - A) BIODEGRADATION BY SOIL MICROORGANISMS
 - B) THERMAL DESTRUCTION (INCINERATION AS WASTE)
 - C) BLENDING WITH FUEL OIL OR COAL
 - D) USE AS FUEL -- CEMENT KILNS, MUN. INCIN.
 - E) USE IN ASPHALT
 - F) USE AS DUST SUPPRESSANT -- ROAD OILING.
- 5) ROAD OILING - FINDINGS AND CONCERNS
 - A) 70-75% WASHED AWAY BY RAIN
25-30% VOLATILIZATION, VEHICLE ADHESION
1% LEFT ON ROAD
 - B) OIL MAINLY CONFINED TO TOP ONE INCH
 - C) HIGH CONCENTRATION OF LEAD IN ROAD SURFACE
 - D) HIGH LEVELS OF LEAD IN ADJACENT PLANT LIFE.

THESE FINDINGS BASED ON U.S. STUDY BUT SEVERELY CRITICIZED FOR LIMITED DATA, GENERALIZATIONS, ETC.

RECOMMENDED THAT FURTHER STUDIES BE UNDERTAKEN TO DETERMINE ECOLOGICAL CONSEQUENCES OF OIL RUNOFF.

OTHER CONCERNS

- PNA'S (POLY NUCLEAR AROMATICS) KNOWN CARCINOGENS
- OTHER HEAVY METALS - VANADIUM
 - MANGANESE

ACTION BY TASK FORCE

- PCB'S ALSO IDENTIFIED BY MOE AS SIGNIFICANT COMPONENT OF WASTE OIL IN ONTARIO
- TEKNEKRON CONCERNS OVER: LEAD
PNA
HEAVY METAL
- TEKNEKRON RECOMMENDATION FOR ECOLOGICAL STUDIES ON OIL RUN-OFF

RECOMMENDATION DEVELOPED BY TASK FORCE INCLUDED A PROPOSED BAN ON ROAD OILING.

TASK FORCE RECOMMENDATIONS NOT ACCEPTED BY DEPUTY MINISTER, ENERGY ON GROUNDS THAT INSUFFICIENT EVIDENCE TO SUPPORT BAN.

MOE AND MTC CHARGED TO RESOLVE DILEMMA.

ACTION TAKEN BY MOE & MTC.

1977 - L.S. LOVE STUDY COMMISSIONED WITH
FUNDING THROUGH LOTTERY PROGRAM

1978 - L.S. LOVE STUDY CONTINUES DUE TO POOR
RESULTS IN 1977

MAY 1979

LOVE REPORT FINALIZED AND
SUBMITTED TO MOE.

CONTINUING ACTION BY TASK FORCESPRING

1979

A MEETING WITH ROAD OILERS ASSOC:

- ROAD OILING IN USE AND ENDORSED BY TOWNSHIPS FOR OVER 40 YEARS
- CALCIUM CHLORIDE NOT COMPLETE SUBSTITUTE AND IS MONOPOLY IN ONTARIO AS ONLY ONE SOURCE
- 71 PERSONS PLUS SEASONAL HELP DEPEND ON ROAD OILING FOR LIVELY HOOD
- WHAT WOULD HAPPEN TO 8 MILLION GALS. OF OIL CURRENTLY USED FOR ROAD OILING
- NO SCIENTIFIC EVIDENCE TO INDICATE ROAD OILING UNACCEPTABLE.
- NOT ALL WASTE OIL CAN BE REREFINED AS SOME OF VEGETABLE AND ANIMAL ORIGIN
- SPECIFICATIONS SHOULD BE DEVELOPED BY MOE MTC AND MNR TO REGULATE OPERATORS, QUANTITY AND QUALITY OF OIL USED AND METHOD OF APPLICATION

CONTINUING ACTION BY TASK FORCE

SUMMER, 1979 MEETING WITH WASTE OIL REFINER
BRESLUBE

- NEED TO CONSERVE PETROLEUM RESOURCES
- NEED TO PROTECT ENVIRONMENT
- BAN ROAD OILING

BRESLUBE OPERATIONS

- CURRENTLY, 2.5 MILLIONS GALLONS PER YEAR
- ABOUT 1 MILLION IMPORTED FROM QUEBEC, U.S.
- EXPANSION UNDERWAY
 - 6.0 MILLION GALLONS BY FALL 1979
 - 10 MILLION GALLONS BY MID 1980

I.E. CAN HANDLE ALL WASTE OIL

CONCLUDING ACTION BY TASK FORCE

SUMMER 1979 1) MEETING WITH ALLIED CHEMICAL
RE CALCIUM CHLORIDE

2) MEETING WITH WITCO CHEMICAL
RE 'COHEREX'

3) MEETING WITH M&F CHEMICALS
RE ROAD STABILIZER - CALCIUM LIGNOSULPHONATE

THESE MEETINGS PROVIDED INFORMATION ON ALTERNATIVE
DUST SUPPRESSANTS

SUMMER 1979

1) SHELL CANADA PROPOSAL FOR
REFINERY IN TORONTO

-
WOULD USE THE PHILLIPS HYDROTREATING PROCESS
AND TO BE ON STREAM IN LATE 1980

2) DISCUSSIONS WITH IMPERIAL OIL RE PROPOSED
REFINERY IN SARINA

-
WOULD USE A SPECIAL PROCESS DEVELOPED BY
IMPERIAL AND TO BE ON STREAM IN 1982

CONTINUING ACTION BY TASK FORCE

MAY 1980

MOE REPORT ON EFFECTS OF ROAD
OILING ON PCB ACCUMULATION IN AQUATIC LIFE

- STRONG CIRCUMSTANTIAL EVIDENCE THAT PCB
IN ROAD OIL IS PICKED UP BY FISH AND
MAY BE RESPONSIBLE FOR PCB'S FOUND
IN RESORT AREAS LAKES

ACTION BY MOE

APRIL 1978

'INTERIM GUIDELINES RESPECTING
PCB IN WASTE OILS'

- ROAD OILING 25PPM MAX
- FUEL FORCEMENT KILNS 100PPM MAX
- FOR REREFINING 25PPM MAX

WHERE DO THINGS NOW STAND?

- CONCERNS OVER ROAD OILING PRACTICES
 - LEAD
 - PNA
 - HEAVY METALS
 - PCB
 - HEALTH
 - ENVIRONMENT
- POSITIONS PRESENTED BOTH FOR AND AGAINST ROAD OILING
- SUBSTITUTES FOR WASTE OIL NOT AVAILABLE FOR ALL CASES
- NO WELL DEFINED HEALTH OR ENVIRONMENTAL IMPACTS BUT STRONG CIRCUMSTANTIAL EVIDENCE
- ADDITIONAL REREFINING CAPACITY TO BE AVAILABLE WHICH WILL COMPETE FOR WASTE OIL
- PUBLIC PRESSURES FOR BAN FOLLOWING BAN BY US, EPA
- ROAD OILERS NEED LEAD TIME OF APPROX 1 YEAR AS OIL ACCUMULATED OVER WINTER FOR NEXT SEASON
- SOME MUNICIPALITIES EXPRESSED CONCERN OVER PROPOSED BAN DUE TO INCREASED COST AND NON-AVAILABILITY OF SUBSTITUTES
- ST. LAWRENCE CEMENT NO LONGER ACCEPTING WASTE OIL AS FUEL
- REGULATION ON MOVEMENT OF PCB'S

WHAT IS PLANNED?

WASTE OIL TASK FORCE WILL CONCLUDE ITS DELIBERATIONS SHORTLY AND RECOMMEND:

- 1) MOE TO RESOLVE ROAD OILING POLICY
- 2) WASTE OIL UTILIZAITON NO LONGER A CONCERN DUE TO REREFINERY PROPOSALS

MOE POLICY?

- 1) CONSIDER SPECIFICATIONS ON WASTE OIL TO BE USED FOR ROAD OILING.
 - PCB
 - LEAD
 - VANADIUM
- 2) CONSIDER GUIDELINES ON APPLICATION
 - MAX. APPLICATION RATES
 - PROXIMITY TO WATER BODIES
- 3) CONSIDER RAMIFICATIONS OF SURVEILLANCE
 - MANPOWER RESOURCES
 - FINANCIAL RESOURCES
- 4) CONSIDER ANALYTICAL REQUIREMENTS AND CAPABILITIES

WHEN?

EARLY 1980

**BIOACCUMULATION RATES, ACUTE AND
CHRONIC EFFECTS OF NEW DIELECTRIC
FLUID PRODUCTS ON FISH**

**SUMMARY REPORT FOR
PROVINCIAL LOTTERY PROJECT NO. 77-003-32
1977 - 1980**

by
**GEORGE W. OZBURN,
ALASDAIR D. SMITH
DONALD E. ORR**

**LAKEHEAD UNIVERSITY
THUNDER BAY, ONTARIO**

November 1980

BIOACCUMULATION RATES, ACUTE AND CHRONIC
EFFECTS OF NEW DIELECTRIC FLUID PRODUCTS ON FISH

SUMMARY REPORT
FOR
PROVINCIAL LOTTERY PROJECT NO. 77-003-32
1977 - 1980

by

GEORGE W. OZBURN, PROFESSOR, DEPARTMENT OF BIOLOGY
ALASDAIR D. SMITH, RESEARCH ASSOCIATE, DEPARTMENT OF BIOLOGY
AND
DONALD E. ORR, ASSOCIATE PROFESSOR, DEPARTMENT OF CHEMISTRY.

LAKEHEAD UNIVERSITY
THUNDER BAY, ONTARIO

NOVEMBER, 1980.

TABLE OF CONTENTS

INTRODUCTION	1
DIELECTRIC FLUIDS	2
ANALYTICAL MEASUREMENT	6
CHEMICAL DATA	12
ACUTE TOXICITY	17
REPRODUCTIVE EFFECTS	21
BIOCONCENTRATION: WATER EXPOSURE	25
BIOACCUMULATION: UPTAKE VIA FOOD	30
SUMMARY	36
BIBLIOGRAPHY	37

INTRODUCTION

In 1971, North American sales of polychlorinated biphenyls (PCBs) were restricted to sealed electrical equipment in an attempt to reduce environmental contamination by these residue-forming compounds. Despite this restriction, U. S. air and water monitoring programs carried out between 1971 and 1976 had not detected any decrease in PCB levels. (Walker, 1976). It soon became apparent that even the use of PCBs as dielectric fluids would have to be curtailed if acceptable environmental backgrounds were to be realized. Manufacturers of dielectric fluids were quick to realize this fact and by the mid-seventies several companies were promoting new chemicals as PCB-alternatives for use in transformers and capacitors.

Suitable PCB-substitutes not only had to possess favorable dielectric properties, but also had to be environmentally acceptable. The chemical manufacturers did indeed conduct "in house" toxicological studies of their proposed PCB-replacement chemicals. The data derived from these studies were incorporated into brochures designed to promote the sale of these products. In the scientific literature, however, little or no toxicological data on these chemicals existed.

Recognizing the need for an impartial and comparative investigation on the environmental compatibility of these new

dielectric fluids, the Aquatic Research Group at Lakehead University submitted a proposal in 1976 to the Ontario Ministry of the Environment to conduct an aquatic toxicity study of several of these new products. The proposal was accepted by the Ministry and the study commenced on May 1, 1977.

Although the original proposal called for a study of five PCB-substitutes, only four were evaluated during the three-year period of the study. We had anticipated that reliable analytical methods for these exotic chemicals would be available, either in the scientific literature or from the manufacturers. On the contrary, it was discovered that analytical procedures for extraction and quantification were either poorly documented or virtually non-existent. Consequently, much of the analytical support had to be developed by our own group during the course of the study. In retrospect, a more realistic proposal in terms of the available manpower would have called for an evaluation of only three PCB-substitutes within the specified time period of this study.

DIELECTRIC FLUIDS

The dielectric fluids were chosen in consultation with Ministry of the Environment and Ontario Hydro personnel. It was decided that the compounds investigated would be those

that had met the electrical requirements of Hydro and were, therefore, serious contenders as PCB-replacements in the Province of Ontario.

The chosen chemicals were trichlorobenzene, polydimethylsiloxane, butylated monochlorodiphenyl oxide and isopropyl biphenyl. The PCB, Aroclor 1016, was also chosen as a "benchmark" chemical. Analytical methods for PCBs are well established and the scientific literature is well documented with respect to toxicological effects of PCBs on fishes. Initial work with A. 1016, therefore, gave our research group valuable experience in working with hydrophobic chemicals. It also served as a basis for either developing or improving analytical techniques for the new dielectric fluids and as a reference compound to compare the environmental suitability of the proposed replacement chemicals.

1. Aroclor 1016 (PCB)

Aroclor 1016 is a capacitor fluid manufactured by Monsanto Chemical Company. It is a polychlorinated biphenyl (PCB) consisting of a mixture of 56% trichlorinated biphenyl, 21% di- and tetrachlorinated biphenyl and less than 1% of mono- and pentachlorinated biphenyl. Fig. 1 is the structural formula for A. 1016.

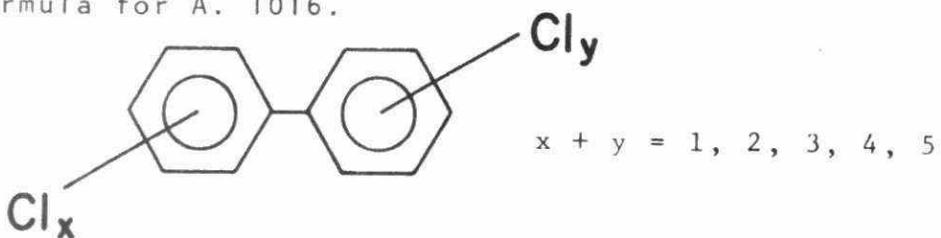
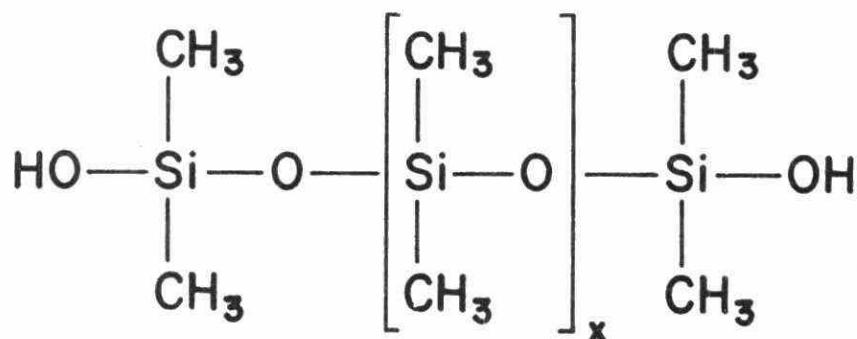


Fig. 1. Structural formula for Aroclor 1016.

2. Polydimethylsiloxane (PDMS)

Dimethylsiloxane is the basic chemical unit comprising a series of silicone products manufactured by Dow Corning Corporation. Dielectrics in this series are collectively referred to as Dow Corning 200 fluids. These liquid silicones are polydimethylsiloxanes (PDMS), where the repeating polymeric unit (dimethylsiloxane) can be as high as 10,000. In the case of our sample, Dow Corning 561 transformer fluid, the actual degree of polymerization was unknown. Fig. 2 is the structural formula for the 200 series of Dow Corning silicone fluids.



Range of x: 0 to 10,000

Fig. 2. Structural formula for Dow Corning 200 fluids.

3. Trichlorobenzene (TCB)

Trichlorobenzene (TCB) is a common organic compound which exists in three isomeric forms: 1, 2, 3 - TCB; 1, 2, 4 - TCB; and, 1, 3, 5 - TCB. Under normal conditions, the 1, 2, 3 - and 1, 2, 4 - isomers are liquids whereas 1, 3, 5 - TCB is a

solid. The trichlorobenzenes possess favourable dielectric properties and General Electric Corporation markets a technical grade mixture of 33% 1, 2, 3 - and 66% 1, 2, 4 - TCB as a transformer fluid. In the Province of Ontario, technical grade TCB has been used to "top up" existing PCB - filled transformers. Fig. 3 is the structural formula for TCB .



Fig. 3. Structural formula for Trichlorobenzene

4. Monochloromonobutylidiphenyl oxide (C_4ClDPO).

The Dow Chemical Company manufactures and markets a capacitor fluid under the trade name, Dow Dielectric Fluid C4. The major component of C4 fluid is monochloromonobutylidiphenyl oxide (C_4ClDPO) , with lesser amounts of monochlorodiphenyl oxide and monochlorodibutylidiphenyl oxide. Smaller amounts of monochlorotributylidiphenyl oxide (<5%) are also present. The actual percentage of these compounds in the capacitor fluid is unknown. Our sample consisted of the major component of C4 fluid, C_4ClDPO , with trace amounts of ClDPO present. Fig. 4 is the structural formula for C_4ClDPO .

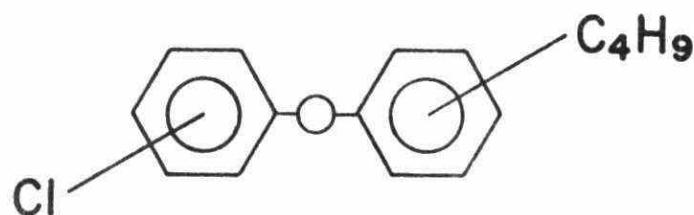


Fig. 4. Structural formula for Monochloromonobutyldiphenyl oxide.

5. Isopropylbiphenyl (IPB).

Westinghouse Electric Corporation markets a capacitor fluid under the trade name, Wemcol. Chemically, Wemcol is isopropylbiphenyl (IPB). Although Wemcol is advertised as 100% IPB, we found our sample to contain up to 1% di-isopropylbiphenyl. Fig. 5 is the general structural formula for Wemcol.

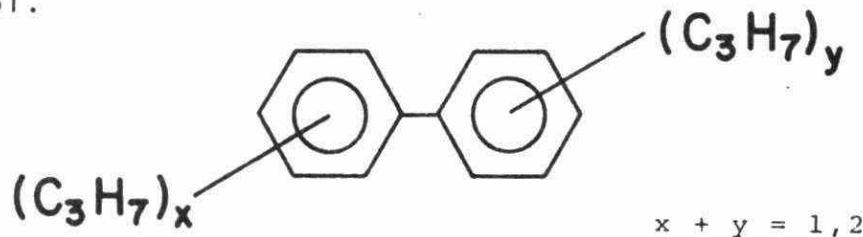


Fig. 5. Structural formula for Wemcol.

ANALYTICAL MEASUREMENT

1. Acetone (C_2H_6CO).

Acetone is widely used as a dispersant or carrier solvent for introducing hydrophobic chemicals into aquatic bioassay systems. We used acetone as the dispersing agent in the present study and hence a method for the analytical measurement of acetone in water was needed.

We employed a colorimetric method involving the production of dinitrophenylhydrazone from 2, 4 - dinitrophenylhydrazine in the presence of ketones (British Drug House, Limited, 1974). Although acetone is thoroughly soluble in water, its' chemical instability and high volatility results in measured quantities of approximately 80% of the nominal concentration.

2. PDMS.

Dow Corning's 561 transformer fluid was originally designated as the first PCB-substitute to be studied. Work began in early May, 1977, to develop an analytical method for recovery and measurement of polydimethylsiloxane (PDMS) in water. No convenient method existed in the scientific literature. However, a method for the determination of PDMS in beer and yeast by infrared spectroscopy was available (Sinclair and Hallam, 1971). Numerous problems were encountered trying to adapt this method to water analysis. PDMS was found to be virtually insoluble in water. In order to obtain measurable amounts of PDMS in water, concentrations of 50,000 mg of acetone per litre were required. An acetone concentration of this magnitude is lethal to fish, being more than six times greater than the LC₅₀ value.

The low solubility problem was further complicated by the high affinity of PDMS for glass. Reproducible extractions were rarely obtained due to adherence of the silicone product to the analytical glassware. Considerable time was spent trying to rid the glassware of silicone contamination.

We found that a combination of multiple washings with ether and oven annealing at 570° C was the only effective method for removing PDMS from glass. This procedure, of course, could not be used to clean the bioassay system. If PDMS was to be studied first, the diluter and test tank system would have to be discarded and rebuilt. After discussions with MOE personnel, it was decided that the technical problems were too great to solve within the time period allotted for this chemical. PDMS, therefore, was placed at the end of the list. If time permitted we would return to the study of PDMS after completing our investigations of the other dielectric fluids.

3. A.1016, TCB, C₄C1DPO, and IPB

The remaining chemicals were all amenable to analytical measurement by gas chromatography.

A Hewlett-Packard 5730A gas chromatograph equipped with both electron capture (ECD) and flame ionization (FID) detection modes was purchased as an instrument dedicated solely to the dielectric fluids project. Table 1 summarizes the gas chromatographic (GC) conditions employed for the analytical measurement of the remaining four dielectric fluids.

A.1016 was not included in the original proposal. It was added to the list as a reference chemical at the request of Dow Chemical personnel. The rational was that the inclusion

TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS FOR ANALYTICAL MEASUREMENT^{*a}

DIELECTRIC FLUID ANALYZED	COLUMN PACKING AND SUPPORT PHASE	DETECTOR USED FOR ANALYSIS	DETECTOR/INJECTOR TEMP. (°C)	CARRIER GAS/PRESSURE (PSI)	CARRIER GAS FLOW (ML/MIN)	COMPONENT RETENTION TIMES (MINUTES AND SECONDS)
A.1016	3% QF-1, 3% DC-200, ON GASCHROM Q	ECD	300/250	5% ARGON IN METHANE/60	50	CHLORO. 7:20 DICHLORO. 9:20 TRICHLORO. 12:00 TETRACHLORO. 14:20 PENTACHLORO. 16:50
TCB	8% BENTONE-34, 10% DC-200, ON GASCHROM Q	ECD	300/250	5% ARGON IN METHANE/60	50	1, 2, 4-TCB 2:10 1, 2, 3-TCB 5:00
C ₄ C ₄ DPO	5% UCW-98 ON GASCHROM Q	FID	300/150	N ₂ /60	40	C ₄ DPO 7:30 C ₄ C ₄ DPO 8:25
	3% OV-210, ON CHROM. W	FID	300/150	N ₂ /60	25	MONO-IPB 9:00 DI-IPB 9:36

* a) INSTRUMENT: HEWLETT-PACKARD, MODEL 5730A

of a dielectric fluid with established analytical procedures and well documented biological effects would serve as a "quality control" check on the methods used to generate both chemical and biological data on the PCB-substitutes. We were pleased that the Dow people insisted on the inclusion of A.1016 as a benchmark chemical. The key to good analytical backup for bioassay studies of hydrophobic compounds depends heavily upon the efficiency with which these compounds can be recovered from water and tissue samples. Dow provided us with excellent extraction methods for PCBs and this information served as a basis for the development of efficient extraction procedures for TCB, C₄C1DPO and IPB.

The extracting solvent was hexane, rather than ether which was suggested in the original Dow method for PCBs. Our studies indicated that both solvents were equally efficient in extracting the PCB-substitutes from water. Hexane had the advantages of being cheaper and less hazardous than ether.

The following general outline summarizes the procedure employed for extracting TCB, C₄C1DPO and IPB from water. In all cases, the water sample size was 250 ml. The volume of hexane varied slightly, however, depending upon concentration and ease of extraction:

- a) A 250 ml sample of water was taken from the midpoint of the test tank. Care was taken not to include any surface water or bottom sediment.

- b) The sample was placed in a 500 ml separatory funnel and a predetermined volume of hexane was added.
- c) The funnel was shaken at maximum speed on a mechanical shaker for 20 minutes.
- d) The water/hexane mixture was allowed to separate and the hexane phase (containing the dielectric fluid) was tapped off.
- e) If necessary, the hexane extract was concentrated by reducing the volume by evaporation over a hot water bath.

Extraction of dielectric fluids from fish tissues was somewhat more complicated. Again, our method was a modified version of the Dow procedure for PCBs:

- a) A whole fish was placed in 20% methanolic KOH at 50°C for 20 minutes.
- b) The resulting digest was extracted with a predetermined volume of hexane in a separatory funnel by mechanical shaking.
- c) The hexane extract (containing the dielectric fluid and lipid material) was allowed to separate from the caustic solution for 15 minutes.
- d) The extract was tapped off and dried over Na_2SO_4 .

e) The extract was then evaporated over a hot water bath to 2 ml, applied to a Florisil column and eluted with 0.5% ether in hexane.

The resulting hexane extracts from both water and tissue samples were injected directly into the GC. Standard curves were developed for each dielectric fluid by injecting hexane standards containing known concentrations of the chemical. Extraction efficiencies from both water and tissue were determined by spiking clean samples with known concentrations of dielectric fluid and comparing the GC response to the standard curve. In cases where the extraction efficiency was less than 100%, correction factors were calculated and used to adjust the measured concentration. By varying the volume of hexane, an optimum extraction efficiency could be obtained for each dielectric fluid. This enabled us to keep correction factors as small as possible when it was necessary to use them.

When concentration of the GC sample was necessary, tests were done to ensure that no significant loss of dielectric fluid occurred during evaporation of the hexane extract.

CHEMICAL DATA

1. Water Solubility.

The scientific literature contains numerous methods for

determining the solubility of hydrophobic organic compounds in water. The problem is that no two methods will yield the same result. According to the ASTM, no acceptable standard method exists. Although this is perhaps a problem for the chemists to solve, aquatic toxicologists must at least try to address it. It is not unusual to see published papers on aquatic bioassay studies of hydrophobic chemicals in which the author attempts to hide the solubility problem in a mass of biological data or ignore it completely. Our experience with the dielectric fluids study has convinced us how critically important a reliable method for water solubility is in generating meaningful bioassay results.

Our attempts to develop a useful relevant method for determining water solubility have been presented in detail in a recent publication (Todd et al., 1979). The following general outline summarizes our method of choice, which we think most closely approximates the physical/chemical conditions in our flow-through bioassay systems:

- a) 500 ml of distilled water is super-saturated with the hydrophobic chemical and stirred at medium speed on a magnetic stirrer for 24 hours.
- b) eight, 50 ml aliquots of water are removed and centrifuged at 15,000 rpm and 18°C for 90 minutes.

- c) 25 ml of supernatant is removed from each centrifuge tube.
- d) two sets of four, 25 ml samples are combined to give two, 100 ml samples.
- e) the samples are then extracted once with 30 ml of hexane, and once with 20 ml of hexane; both extractions use a 2-minute, mechanical shake.
- f) the hexane extracts are then concentrated to 1 ml and injected into the GC.

Table 2, entitled "Chemical Data", summarizes our solubility values for TCB, C₄C1DPO and IPB using the above method. Other solubility figures, extracted from the scientific literature, have been included for comparison. It is readily apparent that there is tremendous variation in these data. It is not surprising, therefore, that similar variations in biological responses are reported by different investigators studying the same hydrophobic chemicals.

2. Octanol/Water Partition Coefficient.

Table 2 also summarizes the octanol/water partition coefficients determined in our laboratory for TCB, C₄C1DPO and IPB. Again, values extracted from the literature have been included for comparison.

The octanol/water partition coefficient ($\log P$) is an important parameter for predicting the biological effects of organic chemicals from physical properties through the use of structure - activity correlations (Veith and Konasewich, 1975).

TABLE 2.

CHEMICAL DATA

WATER SOLUBILITY IN MG/l (PPM) AND OCTANOL/WATER PARTITION COEFFICIENT (LOG P)

DIELECTRIC	SOLUBILITY	O/W PI	SOURCE
A. 1016	0.054	-	BRANSON, 1977.
	0.100	-	MERCIER, 1977.
	-	5.9	VEITH ET AL., 1979.
PDMS	INSOLUBLE	-	ROWE, SPENCER, BASS, 1948.
TCB	0.478	4.7	
	-	4.2	VEITH ET AL., 1979.
C ₄ C ₁ DPO	0.026	4.7	
	0.140	4.2	BRANSON, 1977.
IPB	0.051	7.0	
	10.0	-	MERCIER, 1977.
	-	4.6	KENAGA, 1980.

Use of the log P value for estimating the bioconcentration potential of organics in fish has been demonstrated by Neely et al., (1974). We determined log P values simply as a check on the validity of our bioconcentration data, particularly our calculations for bioconcentration factor (BCF).

Although there are sophisticated methods such as high pressure liquid chromatography (HPLC) for measuring log P (Veith et al., 1979), we used the following classical method:

- a) weighed out into four, 50 ml volumetric flasks, 500 mg lots of dielectric fluid.
- b) filled flasks to 50 ml mark with purified n-octanol.
- c) shook each 50 ml lot with 200 ml of water for 15 minutes on a mechanical shaker at medium speed.
- d) transferred 40 ml of water to each of 2 centrifuge tubes and centrifuged for 90 minutes at 5°^C and 12,000 rpm (8 tubes, total).
- e) took 25 ml samples of the water from each tube and combined two, 25 ml samples to give 50 ml.
- f) extracted the 50 ml samples with 20 ml of pure hexane for 5 minutes (mechanical shake).
- g) concentrated the hexane to 1 ml and injected into the GC.

Log P is calculated as the ratio of the concentration of the chemical in the octanol to the concentration in the water.

Chemicals with large values for log P have greater bioconcentration potential and thus greater BCFs than those with small log P values. From Table 2, our determinations of log P indicate that IPB has the largest value and should yield the largest BCF in a bioconcentration test. TCB and C₄CIDPO have similar log P values and hence, should have similar BCFs. The BCF for A.1016 should be less than that of IPB but greater than TCB and C₄CIDPO.

ACUTE TOXICITY

Standard 96-hour flow-through toxicity tests were conducted according to the methods described by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). The flow-through system has been previously described (Smith *et al.*, 1977). American flagfish (*Jordanella floridae*) were used as the test species and tests were conducted on both adults and fry. Water temperatures were maintained at 25 \pm 1°C and dissolved oxygen levels were kept above 6.9 mg/l at all times.

Nominal chemical concentrations conformed with a recommended concentration series (Sprague, 1973). The chemicals were introduced at least 24 hours before adding the fish. Water samples (250 ml) were analyzed for actual (measured) chemical concentration prior to introducing the fish and every 24 hours thereafter, throughout the duration of the test (i.e. N=5). Data were analyzed by computer, utilizing an LC₅₀ program developed by Stephan (1977). The program subjects the

concentration/mortality data to a series of progressively more sophisticated statistical tests: 1) a simple binomial test; 2) the moving average test; and, 3) the probit analysis (if the concentration gradient tested produces at least two partial kills). The probit analysis, of course, is the most powerful test and hence yields the best estimate for the LC_{50} . Stephan's computer program is entirely based on criteria established by the Committee on Methods for Toxicity Tests with Aquatic Organisms (1975) and hence, is compatible with the test methodology which we employed.

1. Acetone

No LC_{50} value for acetone against our test species, flagfish, could be found in the literature. It was therefore, necessary to establish the acute toxicity of the dispersing agent in order to determine what concentrations could be safely used to introduce the dielectrics into the test system. Our estimates of the LC_{50} for acetone (Table 3) agree well with the value reported for bluegills (Cairns and Scheier, 1968).

On the basis of these tests, we initially chose an acetone carrier concentration of 79 mg/l (100 μ l/l) which is less than 1% of the LC_{50} estimate. However, the dielectric fluids exhibited such poor water solubility that we increased the carrier concentration to 196 mg/l. This concentration is equivalent to 2.3% of the LC_{50} value.

2. Dielectric Fluids

Table 3 compares the acute toxicity of the dielectric fluids we investigated. Where no acute data on a particular fluid was generated, literature values have been included. Table 3 also compares our data to that of other investigators who have determined LC_{50} values for some of these dielectrics.

Great care must be taken in the interpretation of the data presented in Table 3. The test method (i.e. static or flow-through), the species and age of the fish, and the water temperature are all important factors which contribute to the observed biological response (i.e. mortality). Perhaps the most important factor, however, is the water solubility of the chemical. Nearly all of the LC_{50} values listed in Table 3 are greater than the reported solubilities (Table 2).

The classic acute toxicity test assumes that the toxic substance is in true solution. In the case of hydrophobic chemicals like dielectric fluids, solutions above the saturation point are usually involved. Mortality, therefore, is not only a function of the dissolved portion of the chemical but also of the undissolved phase. This is probably the reason why reported LC_{50} values for hydrophobic chemicals often vary considerably from one laboratory to another.

TABLE 3.

ACUTE 96-HOUR LC_{50} (mg/l) *

<u>CHEMICAL</u>	<u>FISH</u>	<u>LC_{50}</u>	<u>95% C. L.</u>	<u>METHOD</u>	<u>SOURCE</u>
ACETONE	FLAGFISH: ADULTS	8,496	8,094-8,918	FLOW-THROUGH	CAIRNS AND SCHEIER, 1968
	FRY	7,659	6,989-8,392		
	BLUEGILL ADULTS	8,300	-		
A. 1016	FLAGFISH: ADULTS	0.05	0.04 - 0.07	FLOW-THROUGH	BRANSON, 1977
	FRY	0.04	0.03 - 0.05		
	FATHEAD ADULTS	0.76	0.58 - 1.02		
PDMS	BLUEGILL ADULTS	>10,000	-	STATIC	HOBBS, ET AL, 1975
TCB	FLAGFISH: ADULTS	3.18	2.88 - 3.51	FLOW-THROUGH	
	FRY	2.17	1.98 - 2.39		
C_4C_1DPO	FLAGFISH: ADULTS	> 2.24	-	FLOW-THROUGH	
	FRY	0.67	0.28 - 1.62		
IPB	FLAGFISH: ADULTS	> 0.75	-	FLOW-THROUGH	MERCIER, 1977.
	FRY	0.28	0.22 - 0.37		
	BLUEFILL ADULTS	4.00	-		
	TROUT FINGERLINGS	2.50	-	STATIC	" "

* CONCENTRATION OF ACETONE CARRIER = 196 mg/l (2.3% OF THE LC_{50})

When the LC_{50} value for a hydrophobic chemical is within the same concentration range as its water solubility, we can be reasonably confident that the LC_{50} is a valid number. For example, our LC_{50} determined for A.I016 (0.05 mg/l) falls well within the reported solubility range of 0.054 to 0.1 mg/l (Branson, 1977; Mercier, 1977). At the other end of the scale, the reported LC_{50} for TCB, 3.18 mg/l, is approximately six times greater than the reported solubility. It becomes somewhat difficult, therefore, to interpret the usefulness and perhaps even the relevance of an LC_{50} value such as that reported for TCB.

REPRODUCTIVE EFFECTS

TCB, C_4 CIDPO and IPB were investigated with respect to their effects on reproduction in flagfish.

Five-level, sublethal concentration gradients for individual dielectrics were established on the basis of their LC_{50} values. With this exception, the testing protocol was identical for all three chemicals.

Juvenile flagfish were randomly distributed among duplicate spawning tanks. Each tank received 15 fish. All fish were maintained in non-dosed, control water during a one-month growth and maturity period.

Following maturation, the fish were selectively culled to

a ratio of 5 females to 2 males per tank, and spawning substrates were introduced. Once synchronous spawning in all test tanks was achieved, dielectric fluid addition was initiated.

The concentration of acetone carrier was 196 mg/l. Controls (water and acetone) were included in each test. Stable chemical concentrations were reached within the initial 24-hour dosing period. Water samples (250 ml) were analyzed 5 days per week from alternate, duplicate tanks at each test level. This sampling procedure and analysis continued throughout the duration of the test.

Spawning substrates were removed daily and examined for eggs. Clean substrates were immediately substituted. Eggs were separated from the substrate and counted. Unfertile eggs and "shells" were discarded. A maximum of 50 viable eggs from each spawning were placed in individual egg cups. Cups were attached to a rocker arm assembly and the eggs incubated in their respective progeny tanks. Excess eggs from water control were also incubated at all test levels. Two hundred eggs per test level were used in this control transfer experiment. Following hatching of the control transfer eggs, 50 fry from each test level were transferred to the spawning tanks and held for fry survival testing.

Differences in egg production and hatching success at different concentrations of dielectric fluid were tested for

significance by a one-way Analysis of Variance. If a significant F-ratio was found, a Duncan multiple range test (Duncan, 1955) was employed to determine which test concentrations yielded significantly different results. Fry survival was subjected to Chi-square analysis.

Spawning periods ran for 21 consecutive days. Fry survival was evaluated over 10-day periods.

Measured concentrations of TCB were approximately 50% of the nominal concentrations; IPB and C_4 CIDPO averaged 40% and 30%, respectively. Measured concentrations, therefore, were in agreement with the order of solubility: TCB > IPB > C_4 CIDPO.

No adult mortality occurred in the TCB and C_4 CIDPO tests during the spawning period (21-day exposure). However, adult mortality did occur in the IPB test. Three fish died at 0.42 mg/l, 1 fish at 0.2 mg/l and 1 fish at 0.1 mg/l.

Table 4 lists the important reproductive parameters and the threshold concentrations for TCB, C_4 CIDPO and IPB at which these reproductive stages were impaired.

C_4 CIDPO had the most overall detrimental effect on reproduction in flagfish. Although TCB caused spawning impairment at a lower concentration than IPB, fry were able to survive higher concentrations of TCB than IPB. As expected, the egg stage was most resistant to all three dielectrics.

TABLE 4. REPRODUCTIVE EFFECTS

DIELECTRIC FLUID	THRESHOLD SPAWNING IMPAIRMENT IN MG/ℓ	THRESHOLD HATCHING IMPAIRMENT IN MG/ℓ	FRY SURVIVAL (10-day EXPOSURE) IN MG/ℓ
TCB	0.29	1.71	1.41
C ₄ C ₁₀ DPO	0.054	0.22	0.023
IPB	> 0.42	> 0.47	0.43

Again, water solubility must be considered in evaluating the effects of these dielectrics on fish reproduction. For TCB and C₄CIDPO, spawning impairment was observed at concentrations within the same order of magnitude as the compounds' solubility. IPB had no effect at concentrations 100 times greater than its solubility and hence, could be considered as the least detrimental to flagfish reproduction.

BIOCONCENTRATION: WATER EXPOSURE

Full-scale bioconcentration tests were conducted with TCB, C₄CIDPO and IPB, but only the TCB and IPB tests were successful. A number of analytical problems resulted in a failure to generate useable bioconcentration data for C₄CIDPO. These problems included: 1) poor GC sensitivity in the FID mode; 2) poor extraction efficiency from both water and tissue samples; and, 3) extremely low water solubility which made stable test concentrations over long periods of time almost impossible.

The test protocol was in accordance with the Proposed Standard Practice for Measuring Bioconcentration of Chemicals with Fishes (American Society for Testing and Materials, 1978).

Juvenile flagfish (approximately 6 months old) were randomly distributed among six (3 duplicate) spawning tanks. Each tank received 48 fish. One set of duplicates served as a control, one set as the "low exposure" group, and one set as the

"high exposure" group.

Test fish were initially exposed to the dielectric fluid for a 28-day uptake period. During this uptake phase of the test, six fish (3 per duplicate tank) were sampled at both test levels (and control) for body burdens of dielectric after 1, 3, 7, 14, 21 and 28 days of exposure. Sacrificed fish were randomly selected and killed by over-dosing with MS-222.

The remaining fish were transferred to a clean flow-through system for a 14-day depuration period. During this phase of the test, six fish (three per duplicate tank) were sampled at both test levels (and control) for body burdens of dielectric after 1, 2, 3, 4, 5, 7, 10 and 14 days. Again, fish were randomly selected and killed by over-dosing with MS-222.

During uptake, water samples (250ml) were taken daily (except week-ends and holidays) from all six tanks and analyzed for dielectric fluid concentration. In the TCB test, the low exposure averaged 1.5 $\mu\text{g/l}$ while the high exposure averaged 9.6 $\mu\text{g/l}$. In the IPB test, average concentration levels were 3.5 $\mu\text{g/l}$ (low) and 24.1 $\mu\text{g/l}$ (high).

The concentration of acetone carrier in both tests was 98 mg/l .

Data collected on water and tissue concentrations of dielectric fluid were analyzed by a computer program called Biofac. The program, developed by Dow Chemical Company, has been documented by Blau and Agin (1978).

Biofac utilizes estimates of three important parameters derived from the time-concentration data: 1) the uptake rate constant, K_1^0 ; 2) the clearance rate constant, K_2^0 ; and, 3) the heteroscedasticity parameter, γ^0 . The program then iteratively searches for better values until the optimal values, K_1^* ; K_2^* and γ^* are found. From these optimal values, Biofac then calculates: 1) the bioconcentration factor (BCF); 2) the depuration half-concentration ($T_{1/2}$); and, 3) the time required to reach 90% of steady state (T to 90% S/S).

Table 5 summarizes our bioconcentration data for TCB and IPB. For comparison purposes, similar data on C₄C1DPO and tetrachlorobiphenyl (a component of A. 1016) have been included in the summary. Measured BCFs have been calculated by Biofac from real time-concentration data. Estimated BCFs have been calculated using the log P value (i.e. octanol/water partition coefficient). No information on the bioconcentration of PDMS could be found in the literature.

An erroneous Biofac analysis for IPB was presented in an interim report on Wemcol (June, 1980). A programming error was discovered which resulted in a re-run of the Biofac analysis. The raw data was also sent to Dow Chemical for a Biofac analysis, to confirm our newly-generated data:

TABLE 5. BIOCONCENTRATION: WATER EXPOSURE

DIELECTRIC FLUID	UPTAKE $\lambda/g/d$	CLEARANCE $\lambda/g/d$	STeady STATE	Days to 90% CLEARANCE	Days to 50% CLEARANCE	BCF MEASURED	BCF ESTIMATED	SOURCE OF REFERENCE
TETRACHLOROBIPHENYL*a	286	0.03		215.0	-	9,550	-	Branson, 1977
TCB	1,110	1.21		1.91	0.58	921	-	Veith <u>et al.</u> , 1979
	-	-		-	-	-	1,753	
C_4ClDPO	142	0.50		4.63	1.38	292	-	Blanchard <u>et al.</u> , 1977
	-	-		-	-	-	756	Veith <u>et al.</u> , 1979
IPB	698	0.24		9.55	2.88	2,896	-	Kenaga, 1980
	-	-		-	-	-	1,088	

* a) 21% COMPONENT OF A.1016

NEW BIOFAC ANALYSIS - IPB

PARAMETER	UNITS OF	LOW EXPOSURE	HIGH EXPOSURE
MEASURED	MEASUREMENTS	(3.51 μ g/l)	(24.06 μ g/l)
K_1^*	1/g/day	698	4611
K_2^*	days ⁻¹	0.24	0.43
$T_{\frac{1}{2}}$	days	2.88	1.61
BCF	-	2896	10790
T to 90% S/S	days	9.55	5.32
ζ^*	-	0.388	1.866

Water concentrations used in the Biofac analyses reported in Table 5 were all in the 1 - 5 μ g/l range. Similar exposure levels, therefore, render the data on all four dielectrics comparable.

The rates of uptake are in the order: TCB > IPB > tetrachlorobiphenyl > C_4 C1DPO; clearance rates are in the order : TCB > C_4 C1DPO > IPB > tetrachlorobiphenyl. Although TCB exhibits the fastest bioconcentration rate, it is also more rapidly excreted and/or metabolized than the other dielectric fluids. At the other end of the scale, the PCB (tetrachlorobiphenyl) exhibits both slow uptake and clearance. The times to 50% clearance for TCB, C_4 C1DPO and IPB were all within three days. Although this parameter is not reported for tetrachlorobiphenyl, the clearance rate constant for this PCB indicates that it would take 10-50 times longer for body burdens to be equivalently reduced.

The PCB, of course, has the highest measured BCF. Measured BCFs for TCB and IPB were about one order of magnitude lower. C_4 C1DPO was about two orders of magnitude lower than the PCB. Estimated BCFs (calculated from log P values) are in the same order of magnitude as those derived from real time-concentration data (i.e. measured BCFs).

BIOACCUMULATION: UPTAKE VIA FOOD

To compliment the water exposure tests with flagfish, we applied a novel experimental approach to study the bio-accumulation dynamics in rainbow trout (*Salmo gairdneri*) fed diets containing PCB-substitutes. Although this unique experimental method was attempted with TCB, C_4 C1DPO and IPB, only the TCB experiment was successful. Again, analytical problems with C_4 C1DPO and IPB were partly to blame for the failure of these experiments. Poor detection capability of the GC in FID mode forced us to use high concentrations of these dielectric fluids in the diet. This caused toxic effects on the fish, which in turn, disrupted their normal metabolic processes. Data was so sporadic that it was rendered useless. Another problem with the C_4 C1DPO and IPB experiments was the discovery of background residues (probably pesticides) in both the trout stock and the commercial trout feed. These residues were often present in such large amounts that they completely

masked the dielectric fluid on the chromatograms.

These problems were not encountered in the TCB experiment. The mode of detection employed for GC analysis of TCB is ECD, which has far superior sensitivity. Also, no background residues were detected. Thus, although residues were probably present in the TCB experiment as well, they did not cause interference in the GC analyses. The technique used in the TCB/food experiment was developed at the National Research Council of Canada. It involved the incorporation of a radioactive chemical marker, ^{203}Hg - labeled methyl mercury in the diet, in addition to the chemical of interest (i.e. TCB).

The rationale underlying the method has been discussed in detail by Gidney *et al.* (1980) and Roberts *et al.* (1977). In practice, a group of fish is given a single feeding or "pulse dose" of contaminated ration. A postdose series of whole-body gamma counts, obtained by the method of Ruohula and Miettinen (1975), is then used to construct a curve of the assimilation and clearance of the radioactive marker (Fig.6). In Figure 6, the upper curve represents whole-body retention of the marker (^{203}Hg) as a function of time. E is the initial count obtained after the feeding of a single meal labeled with both marker and chemical of interest (i.e. TCB).

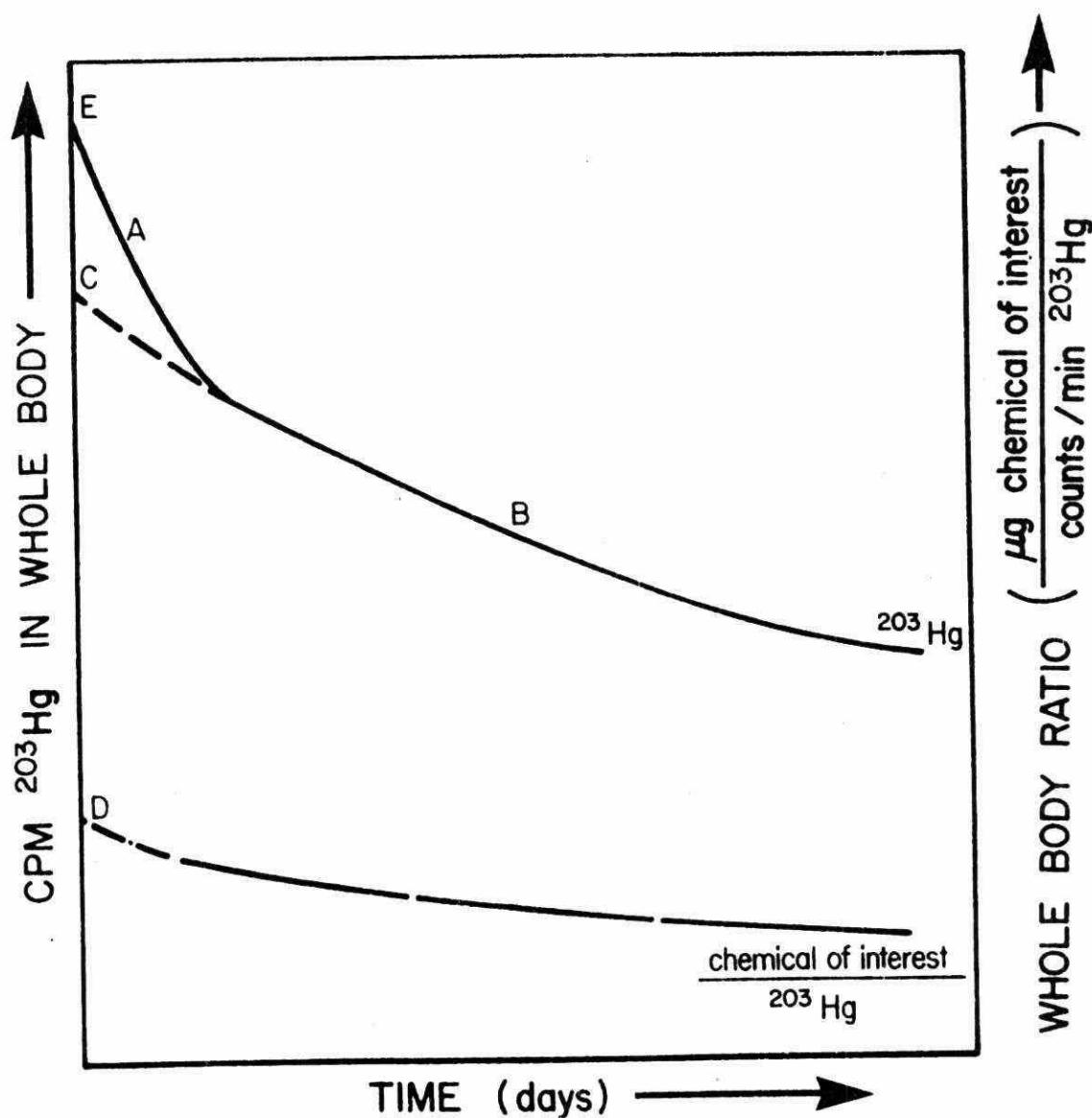


Fig. 6. An illustration of two-compartment clearance of ^{203}Hg - labeled methyl mercury and its application in estimating the assimilation efficiency of any chemical of interest (modified from Gidney *et al.*, 1980).

Slope A represents clearance of the ingested dose of marker not absorbed from the gut tract. Slope B represents clearance of the marker sequestered in tissues. C is obtained by extrapolation of Slope B and is an estimate of the amount of marker sequestered in the tissues at zero time. The ratio C/E is an estimate of the net assimilation efficiency for the marker from the gut tract into the body tissues.

The lower curve represents the ratio of the amount of TCB in the fish to the whole-body count as a function of time. The ratios are calculated from direct measurements of ^{203}Hg and TCB determined on groups of fish sacrificed sequentially after voidance of the contaminated meal. D, obtained by extrapolation, is an estimate of the initial ratio. The net assimilation efficiency for TCB can be calculated from the initial ratio, D, the net assimilation efficiency of the ^{203}Hg , C/E, and the actual ratio of TCB to ^{203}Hg in the ration.

The clearance of TCB from individual fish is calculated from the tissue concentration at the time of sacrifice and the estimated quantity initially sequestered in the tissues at zero time.

The experiment employed a ration containing 50 $\mu\text{g/g}$ of TCB. The assimilation efficiency and the percent of TCB cleared at several postdose times were then determined.

Complete details of the TCB experiment have been published (Smith et al., 1980). Table 6 summarizes the relevant data obtained in this study. Rainbow trout had an assimilation efficiency for TCB of 61%. The data suggest that TCB is readily absorbed from the gut tract. However, the trout were able to clear (i.e. excrete and/or metabolize) 95% of the TCB body burden in less than 8 days. The estimated time to 50% clearance was about 4 days. Thus, this data reflects the same pattern that was found in the water exposure experiment: TCB is both rapidly accumulated and rapidly eliminated by fishes.

TABLE 6. BIOACCUMULATION: UPTAKE VIA FOOD

DIELECTRIC FLUID	TCB IN FOOD, mg/g (ppm)	ASSIMILATION EFFICIENCY, %	DAYS TO 95% CLEARANCE (MEASURED)	DAYS TO 50% CLEARANCE (ESTIMATED)
TCB	50	61	7.25	3.82

SUMMARY

The Aquatic Research Group at Lakehead University has generated some useful and unbiased information with respect to the PCB-substitute compounds studied:

1. efficient extraction techniques for water and tissue samples, and optimum conditions for analytical measurement.
2. a preferred experimental method for determining water solubility.
3. acute toxicity and reproductive effects, and whether or not these effects were within saturation levels (i.e. water solubility ranges).
4. bioconcentration potential, determined from both physical/chemical correlations and actual water (and food) exposure tests.

BIBLIOGRAPHY

American Society for Testing and Materials. 1978. Proposed standard practice for measuring bioconcentration of chemicals with fishes. ASTM - Draft No. 8. *American Society for Testing and Materials, Philadelphia* (unpublished).

Blanchard, F. A., I.T. Takahashi, H. C. Alexander and E. A. Bartlett. 1977. Uptake, clearance and bioconcentration of ¹⁴C - sec-butyl - 4 - chlorodiphenyl oxide in rainbow trout. *Aquatic Toxicology and Hazard Evaluation, ASTM STP 634*, F. L. Mayer and J. L. Hamelink, Eds., *American Society for Testing and Materials, Philadelphia*, pp. 162-177.

Blau, G. E. and G.L. Agin. 1978. A User's Manual for Biofac: A computer program for characterizing the rates of uptake and clearance of chemicals in aquatic organisms. *The Dow Chemical Company, Midland*. (Lab Report).

Branson, D. R. 1977. A new capacitor fluid — A case study in product stewardship. *Aquatic Toxicology and Hazard Evaluation, ASTM STP 634*, F. L. Mayer and J. L. Hamelink, Eds., *American Society for Testing and Materials, Philadelphia*, pp. 44-61.

British Drug House, Limited. 1947. The BDH Book of Organic Reagents for Analytical Use. *BDH Laboratory Chemicals Group, Poole, Dorset*, p. 56.

Cairns, J. and A. Scheier. 1968. A comparison of the toxicity of some common industrial waste components tested individually and combined. *Progr. Fish Cult.* 30:3-8.

Ruohula, M. and J. K. Miettinen. 1975. Retention and excretion of ²⁰³Hg - labeled methyl mercury in rainbow trout. *Oikos*, 26:385-390.

Sinclair, A. and T. R. Hallam. 1977. The determination of dimethylpolysiloxane in beer and yeast. *Analyst*, 96:149-154.

Smith, A. D., T. J. Griffith, D. E. Orr, and G. W. Ozburn. 1980. Assimilation efficiency and clearance of trichlorobenzenes in rainbow trout. *Aquatic Toxicology*, ASTM STP 707, J. G. Eaton, P. R. Parrish, and A. C. Hendricks, Eds. *American Society for Testing and Materials*, Philadelphia, pp. 216-223.

Smith, A. D., J. R. Butler, and G. W. Ozburn. 1977. A pneumatic dosing apparatus for flow-through bioassays. *Water Res.* 11:347-349.

Sprague, J. B. 1973. The ABC's of pollutant bioassay using fish. *Biological Methods for the Assessment of Water Quality*, ASTM STP 528, J. Cairns Jr. and K. L. Dickson, Eds., *American Society for Testing and Materials*, Philadelphia, pp. 6-30.

Stephan, C. E. 1977. Methods for calculating an LC50. *Aquatic Toxicology and Hazard Evaluation*, ASTM STP 634, F. L. Mayer and J. L. Hamelink, Eds. *American Society for Testing and Materials*, Philadelphia, pp. 65-84.

Todd, J., D. E. Orr, and G. W. Ozburn. 1979. The unreliability of solubility data for organic compounds of low solubility in water. *Proc. Sixth Annual Aquatic Toxicity Workshop*, Winnipeg, November, 1979. *Fisheries and Marine Service Technical Report* (in press).

Veith, G. D., D. L. DeFoe, and B. V. Bergstedt. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. *J. Fish. Res. Board Can.* 36:1040-1048.

Committee on Methods for Toxicity Tests with Aquatic Organisms. 1975. Methods for acute toxicity tests with fish, macro-invertebrates, and amphibians. U. S. Environmental Protection Agency, Duluth. Ecological Research Series EPA-600/3-75-006.

Duncan, D. B. 1955. Multiple range and multiple F-tests. *Biometrics*, 11:1-42.

Gidney, M. A. J., J. R. Roberts, and A. S. W. de Freitas. 1980. A technique for estimating individual ingested ration in group fed organisms. *Environ. Sci. Technol.* (in press).

Hobbs, E. J., M. L. Keplinger, and J. C. Calandra, 1975. Toxicity of polydimethylsiloxanes in certain environmental systems. *Environ. Res.* 10:397-406.

Kenaga, E. E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. *Am. Chem. Soc.* 14:553-556.

Mercier, G. E. 1977. Wemcol capacitor fluid development. *Proc. Am. Power Conf.* 39:1043-1051.

Neely, W. B., D.R. Branson, and G. E. Blau, 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environ. Sci. Technol.* 8:1113-1115.

Roberts, J. R., A. S. W. de Freitas, and M. A. J. Gidney. 1977. Influence of lipid pool size on bioaccumulation of the insecticide chlordane by northern redhorse suckers (Moxostoma macrolepidotum). *J. Fish. Res. Board Can.* 34: 89-97.

Rowe, V. K., H. C. Spencer, and S. L. Bass. 1948. Toxicological studies on certain commercial silicones and hydrolyzable silane intermediates. *J. Ind. Hyg. Toxicol.* 30:332-352.

Veith, G. D., N. M. Austin, and R. T. Morris. 1979. A rapid method for estimating log P for organic chemicals. *Water Res.* 13:43-47.

Veith, G. D. and D. E. Konasewich. 1975. Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. *International Joint Commission Publication, Windsor, Ontario.*

Walker, C. R. 1976. Polychlorinated biphenyl compounds (PCB's) and fisheries resources. *Fisheries*, 1:19-25.

FACTORS AFFECTING ACCUMULATION OF ORGANICS IN FISH

G.R. CRAIG

ONTARIO MINISTRY OF THE ENVIRONMENT

LIMNOLOGY & TOXICITY SECTION

ABSTRACT

Historically, biological studies of organics have been limited to pesticides and PCB's. While these compounds continue to be monitored their importance has decreased as a result of controls effected voluntarily or through legislation. Pesticides however, will continue to be important in the study of other organic compounds due to the chemical/physical characteristics that they share.

Pesticides were designed to optimize site specific activity, penetration of target organisms and environmental persistence. Consequently, the environmental effects have included slow degradation, wide spread dispersion, extensive biotic availability and unanticipated sublethal activity in non-target organisms. Additionally the analytical techniques for measurement of pesticides have been well developed allowing longer term evaluation. This analytical advantage is not always shared with industrial organics more recently identified in water, sediment and fish despite advances in gas chromatography and mass spectrometry.

Greater attention is being paid to the structure of organics with respect to their biological activity. Chemical structure is being correlated with characteristics such as solubility, vapour pressure, polarity and octanol-water partition coefficients. Correlations between biological activity and the above chemical characteristics are being used to predict the activity of other organics identified in the environment but not yet studied in the laboratory. The logarithmic function of the octanol-water partition coefficient has been most useful in predicting acute toxicity of compounds to fish and invertebrates. Predictive equations using the partition coefficient of compounds have also been developed to estimate the level of accumulation expected in exposed fish.

The rates of organic accumulation and clearance in fish have been determined in the laboratory so that time to 90% saturation and the half life can be estimated. The presence of better documented pesticides or PCB's in field studies provides a reference for calculating accumulation rates of other compounds. Caged fish can be analysed periodically during exposure then transferred to an uncontaminated area and sampled during clearance to estimate the depuration rate. The ratio of accumulation over depuration rates represents the bio-concentration factor for the compounds identified.

Recognition for the need to assess or estimate the environmental hazard of the numerous organic compounds requires that a variety of predictive techniques be developed. These techniques will unfold through further study of conventional organics and by selecting new study compounds according to measurable structure and physical/chemical characteristics. Although predicting the biological activity of organics does not substitute wholly for actual testing, the increasing resources and complex technology required to complete such assessments virtually prohibits empirical data generation for the many hundreds of compounds identified in receiving waters each year.

THE PROBLEM OF ABANDONED MINES IN ONTARIO:
A CONFRONTATION WITH HISTORY

BY: J.E. DOUGNAN AND J.R. HAWLEY

WASTE MANAGEMENT BRANCH
ONTARIO MINISTRY OF THE ENVIRONMENT

Presented at the Gayline Hotel
November 25, 1986

The mining industry in Ontario has had a long and prosperous history. Its roots can be traced back almost a century before Confederation, when, in 1770, Jesuit Fathers began experimenting and working with native copper at Mamainse Point on the East shore of Lake Superior.

Ontario's mining history up to the late 1950's can be summarized as follows:

- 1800 - First iron furnace erected at Furnace Falls (Lyndhurst) Leeds County
- 1822 - First mining of gypsum from near Paris, Brant County
- 1847 - First reported Canadian occurrence of Uranium Mineral -- near Theano Point on east shore of Lake Superior
- 1848 - Montreal Mining Company started mining copper at Bruce Mines
- 1858 - First commercial oil well in North America opened at Oil Springs, Lambton County
- 1866 - First discovery of gold at Eldorado, Hastings County (Richardson mine).
 - High-grade silver discovered on island in Lake Superior (Silver Islet mine)
 - First production of salt near Goderich, Huron County
- 1870 - First commercial shipments of apatite in Canada from North Burgess Township Lanark County
 - First shipment of graphite from North Elmsley Township Lanark County

1878 - Gold discovered at Lake of the Woods

1883 - Copper nickel ore discovered near Sudbury (Murray mine)

1888 - First smelter blown-in at Copper Cliff
- Discovery of natural gas in Essex County

1896 - Black Donald graphite mine discovered, Renfrew County
- Talc mining started near Madoc, Hastings County

1900 - Lake Superior Power Company commenced production from Helen iron mine at Wawa
- Corundum mining commenced Raglan Township Renfrew County

1903 - High-grade cobalt-silver minerals discovered at Timiskaming
- Town of Cobalt named

1905 - First recorded shipments of Canadian fluorite from Madoc, Hastings County

1906 - Silver discovered at Mt. Lake, gold discovered at Larder Lake

1908 - First discovery of gold in the Porcupine area

1911 - First discovery of gold at Kirkland Lake

1916 - Falconbridge nickel deposits discovered at Sudbury

1925 - Discovery of gold at Red Lake

1931 - Discovery of gold at Little Long Lac

1935 - First production of nepheline syenite at Blue Mountain, Peterborough County

1938 - Discovery of iron ore in bed of Steep Rock Lake

1942 - First production of magnesium in Canada at Haley,
Renfrew County

1944 - Steep Rock Iron Mines commenced shipping of iron
ore

1945 - First production of calcium in Canada at Haley,
Renfrew County

1948 - Rediscovery of uranium at Theano Point, Lake
Superior

1950 - Discovery of Marmoraton iron-ore mine, Hastings
County

- Production of asbestos commenced at Munro mine,
Matheson

1953 - International Nickel attains largest non-ferrous
underground operation in the world at Sudbury

- Discovery of ore-grade uranium deposits at Blind
River

- Discovery of copper-zinc at Manitouwadge

1955 - First uranium ore produced from Blind River

- First contracts for the sale of uranium from the
Bancroft area

- First underground salt mine commenced production
at Windsor.

In 1957 a growing public awareness of ecological
pressures resulting from large scale diverse industrial
activity in the Province prompted the formation of the
Ontario Water Resources Commission. The prime task of the
Commission was to ameliorate waste discharge problems

resulting from active mining operations in Ontario. However, at the same time, it was recognized that a total solution to the problem of mine waste control could not be obtained without control of outstanding problems created by a large number of abandoned properties in the Province.

It took a decade to acquire an understanding of the special mine waste control problems confronting industry and government alike and to develop and implement the technology required to solve the majority of these problems. By 1968, however, an effective abatément function had been firmly established. As a result, more attention could be focussed on the diverse environmental problems presented by Ontario's derelict mining lands.

In the early 1970's the Ontario Water Resources Commission was amalgamated with other government groups and evolved into the present-day Ontario Ministry of the Environment. During this period of time, several major advances were made by the Ministry in areas such as acid mine drainage, the toxicity of mine-mill reagents, the design and siting of tailings disposal sites, and mine-mill waste water recycling. Many comprehensive reports were published and include the following:

- (a) Guidelines for Environmental Control in the Ontario Mineral Industry
- (b) Mine Waste Control in Ontario

- (c) The Use, Characteristics and Toxicity of Mine-Mill Reagents in the Province of Ontario
- (d) The Problem of Acid Mine Drainage in the Province of Ontario
- (e) On Land or Under Water? The Tailings Disposal Problem

In 1977, the Ministry of the Environment received funding from "The Provincial Lottery" Corporation to augment the Ministry's Abandoned Mines Program. This funding gave Ontario a running start on an extensive environmental program which should ultimately remove the threat of contamination from abandoned mines and restore thousands of acres of scarred landscape to their proper natural state. "The Provincial Lottery" funding also enabled the Ministry to publish a 234-page report entitled: "The Chemical Characteristics of Mineral Tailings in the Province of Ontario". This report described, for the first time, the extent of the problem of abandoned mining operations in Ontario and the specific contaminants that must be dealt with.

At the end of 1978, there were 17,073 acres of tailings in the Province that were regarded as still being active (that is, associated with currently active mining companies) and 7,694 acres that were regarded as abandoned. The active areas contained 741,252,000 tons of mineral tailings while the abandoned areas contained an additional

336,100,000 tons. In summary, therefore, at the end of 1978, in Ontario, 1,077,352,000 tons of tailings were contained in areas covering 24,767 acres. These figures are not static, however. Active mining operations in the Province produce over 100,000 tons of new tailings each day and active tailings areas, when filled, are transferred to the "abandoned" category. In fact, the total tonnage given for tailings on the ground in Ontario at the end of 1978 has to be increased by 110,000,000 tons to make it current. Simply put, the volume of mineral tailings produced in Ontario from 1770 to 1978 (208 years) is now being produced in less than 10 years. This rate is accelerating.

Several hundred tailings disposal areas exist in Ontario and these range in size from less than two acres to over 1,000 acres. A common size for these tailings areas is from 50 to 300 acres.

In brief, poorly controlled tailings areas exposed to the atmosphere can give rise to environmental problems which may include one or more of the following:

1. Leaching of contaminants from the tailings with subsequent impairment of downstream areas. Routinely encountered contaminants include undesirable metals, acids, arsenic and radionuclides.

2. Physical deterioration of a tailings area by natural processes such as erosion. Existing tailings dams and decant structures may be weakened to the point of failure. Upon failure, large volumes of contaminated sediment can be carried to downstream areas. In addition, wind can lift contaminated material from the surface of a tailings mass and transport it long distances.
3. Contamination of local groundwater supplies.
4. Contamination of local vegetation and animal life by processes such as metal uptake and bio-accumulation.

Given the fact that significant acreages and enormous volumes of mineral tailings are available, it is not surprising that many attempts have been made to develop large and small scale uses for waste mineral tailings. In fact, due to the great amount of energy required to reduce solid rock to the sandy or silty consistency of tailings, the need to conserve energy supplies and the serious environmental problems that are sometimes created by these deposits, every effort should be made to encourage the re-use of discarded mineral tailings. In addition, in order to help conserve supplies of non-renewable, naturally occurring substances, efforts to win residual mineral values from tailings masses should be encouraged.

In spite of the above statement, some tailings deposits should be regarded as unfit for re-use or as unfit for a particular use due to one or more of a variety of factors. These factors may be physical, chemical, and/or radiological in nature.

The chemical and physical characteristics of any specific tailings deposit depend on the geology and mineralogy of the deposit being mined, the mining method being used and on the milling procedures that are (or were being) followed in order to liberate the required mineral values from the ore. Even within the same mining camp, the chemical and physical characteristics of individual tailings masses often (although not always) vary widely.

Over the years, there have been many notable instances of contaminated discharges from active and abandoned tailings deposits in Ontario. Close examination of these discharges frequently revealed a complex chemical nature that was previously unsuspected.

Given all of the above, the Ontario Ministry of the Environment in the summer of 1977, began its concentrated drive to deal with the problem of abandoned mining operations.

The program, as developed, is being implemented in four discrete stages:

Stage (1) The documentation of all inactive and abandoned mining operations in the Province in terms of location and ownership. Several thousand such properties exist.

Stage (2) The determination, in a preliminary sense, of the environmental impact of specific properties and, in a preliminary sense, the recommendation of remedial measures to be taken at these properties.

Stage (3) The development, as required, of detailed environmental impact assessments for chosen specific properties and the development, as required, of necessary control technologies.

Stage (4) The actual implementation of control measures at chosen specific properties; in other words, the arrangement of Provincial participation in the implementation of remedial measures where the responsible party cannot be identified.

Stage (1) of the program was completed by the end of 1978 in that the inactive and abandoned mining operations in the Province were located and ownership defined when and where possible. Since ownership of these properties changes hands routinely, there is some difficulty in keeping files current.

Stage (2) of the program, that is the determination in a preliminary sense, of the environmental impact of specific properties is currently nearing completion. This stage of the program presented complex difficulties due to an almost complete absence of reliable chemical data relating specifically to Ontario's tailings masses and known tailings masses in general. The Ministry, therefore, had to generate its own data base and this could only be accomplished by carefully sampling all accessible tailings areas in the Province and then subjecting all acquired samples to detailed chemical investigations. In fact, over 4,000 individual tailings analyses, covering 32 different chemical parameters were amassed during the program and formed the basis of the report already mentioned entitled "The Chemical Characteristics of Mineral Tailings in the Province of Ontario". This report serves to indicate areas where potential environmental problems exist. In the summer of 1980, the sampling program was extended to cover areas previously not sampled and to confirm prior results where potential environmental problems were indicated. These new samples, already acquired will be used to determine the radiological characteristics of all Ontario tailings masses, and in fact, have already been subjected to a preliminary gamma radiation screening. Proposed testing will confirm and implement previous results and expand the original data base in that many additional chemical parameters will also be determined.

At this time, the concept of revegetation is a popular and useful solution to many of the problems associated with derelict tailings areas. For this reason, it was considered advantageous to collect samples of any vegetation that was found to exist in harmony with the mineral tailings already sampled. As a result, in 1978, different varieties of vegetation were sampled at 35 inactive and abandoned mineral tailings areas in Ontario, and analysed for 23 different parameters. It was also necessary to collect samples of similar species of vegetation growing in areas removed from the sample sites for use as controls. Similar sampling was completed in the summer of 1980 and a report detailing findings is being undertaken.

With stages (1) and (2) of the project virtually completed, the abandoned mines program is now being accelerated in an attempt to achieve an early resolution of problems of immediate concern.

The first priority of the project involves the reclamation of those abandoned mines or tailings areas that pose immediate or potential hazards to human health or to established communities.

In a strictly theoretical sense, there are few, if any, substances in the universe that can truly be described as "inert". Sooner or later, even the most resistant

substances are conquered by the forces of their environment. Taking this point of view, all the materials found in a tailings area are eventually free to escape the area. The most essential ingredient in this type of approach is the element of time. In most cases, the time required for the dissolutions or reactions to go to completion approximates that of hundreds or thousands of human life spans. On a day-to-day, or short term basis, this approach to environmental problems generated by existing deposits of mineral tailings is not practical except perhaps in a few instances such as those involving specific long-lived radioisotopes. Since the Abandoned Mines Program of the Ministry of the Environment is intended to be a practical program, the reclamation concepts involved are intended to be effective over time periods of perhaps a century or more as opposed to thousands or hundreds of thousands of years. While it is recognized that over periods of hundreds or hundreds of thousands of years, most components of a tailings area including the mineral silicates will undergo some degree of chemical or physical change, it is also recognized that the most common components of the earth's crust will also undergo similar changes given the same physical and chemical conditions. The bulk of the vast majority of tailings masses located in Ontario's hardrock mining district consists of a variety of relatively stable silicates and oxides. From an environmental standpoint,

therefore, we restrict our interest to those mobile elements or substances that commonly occur in tailings areas in above average or abnormal concentrations. With this in mind, the high level of sulphur and arsenic routinely encountered in Ontario tailings areas should be noted. The stresses that can be placed on the environment by these two elements and their associated compounds are well documented. The low level of calcium noted in these tailings areas is also of interest since calcium compounds are, in large part, responsible for the acid neutralizing capacity that any specific tailings mass might have.

As a result, on a Province-wide basis, the two most important environmental problems that are likely to be encountered at Ontario tailings disposal sites are the control of:

- 1) sulphur and sulphur compounds, and
- 2) arsenic and arsenic compounds

The unstable sulphur compounds commonly found in Ontario tailings masses have the ability to spontaneously decompose to liberate large amounts of (sulphuric) acid and associated metals. The local environmental effects of these discharges are routinely devastating and, coupled with the problem of acid rain, can give rise to regional acid problems.

Arsenic, long known for its toxicity to humans, also occurs commonly in a variety of forms in Ontario tailings areas. Arsenic is a mobile substance that responds only grudgingly to accepted forms of waste treatment.

While sulphur and arsenic present us with the most pressing waste control problems at abandoned Ontario mining sites, we are frequently faced with other problems such as the transportation by wind or water of a variety of substances including asbestos; radionuclides such as radium and thorium; mercury, a heterogeneity of metals and non-metals and a perplexing array of residual mine/mill reagents.

In the past, tailings masses in the Province have been characterized as:

- 1) simple sterile soils, and
- 2) as rich deposits of almost every metal.

In reality, neither of the above is strictly true.

Compared to the chemistry of the earth's crust, Ontario tailings areas are routinely:

depleted in substances such as: sodium
magnesium
fluorine
aluminum
phosphorus
chlorine
potassium
calcium
tinanium
manganese
strontium

barium
molybdenum

and enriched in such substances as: nitrogen
vanadium
chromium
iron
cobalt
nickel
copper
zinc
arsenic
selenium
cadmium
tin
antimony
boron
mercury
lead
bismuth
sulphur

There are, of course, individual exceptions to all cases above. The causes, or probable causes of the enrichments or depletions noted can be explained with relative ease in most cases. Explanations involve concepts of mineralogy-geology and intimate knowledge of mine-mill process technology.

In Ontario, it is expected that:

- 1) the reclamation of derelict mining lands will largely be achieved by revegetation. Other methods of stabilization of these areas will have to be used when and where revegetation is not feasible.
- 2) the owner of the land involved, and not the public, will pay for the reclamation of the land, and
- 3) every attempt will be made to achieve a "walk-away" situation upon the completion of reclamation at any

particular property. A "walk-away" situation is exactly what it sounds like: no maintenance and no monitoring.

The reclamation by revegetation of Ontario's abandoned mining properties presents problems that are somewhat obvious but are frequently overlooked by those demanding immediate action in any particular area. For instance:

- (a) Many abandoned areas are quite remote. As such, access to the property can present great difficulties, as can the complete lack of available utilities such as electrical power. In extreme cases, seeding of derelict mining lands may have to be accomplished from aircraft.
- (b) Reclamation by revegetation in most mining areas in Ontario can routinely only be carried out during a few weeks in the spring and perhaps a few weeks in the fall of the year.
- (c) It may take well over 5 years to produce a successful self-sustaining vegetative cover.
- (d) The revegetation of derelict mining lands is a young science and gaps in technology do exist. This is particularly true where acid mining lands are involved.
- (e) It is currently estimated that costs for the reclamation of all abandoned mining lands in the province now exceed 125 million dollars, Canadian.

Up to the present time, jurisdiction in Ontario for the reclamation of mining properties has not rested with the Ministry of the Environment. Instead, all references to reclamation were found in the Ontario Mining Act. As a result, the Waste Management Branch of the Ontario Ministry of the Environment recently moved to transfer this jurisdiction directly to the Ministry of the Environment. This task has been essentially completed.

As a result, an all-encompassing and specific program of reclamation should be possible in the Province of Ontario beginning early in 1981. This program, is expected to include the following:

- (a) All new, active, idle, and abandoned mining operations in the Province of Ontario will report to the Ministry of the Environment within a given period of time concerning their specific abandonment or reclamation programs. These programs should be to the satisfaction of the Ministry of the Environment and should be completed within an agreed to time frame.
- (b) In essence, it is expected that property owners will plant and maintain vegetation or otherwise stabilize all despoiled areas on their property including mine tailings areas, waste rock disposal sites, and any sites containing related debris.

(c) A bonding mechanism is proposed to be used when required to ensure that reclamation procedures are carried out as specified.

In summary, the Abandoned Mines Program of the Ontario Ministry of the Environment has evolved into a precise mixture of investigative research and legislation. With the rapidly rising costs of reclamation, a successful conclusion to the project is deemed both timely and necessary. During 1981, the actual process to transform thousands of acres of sterile waste land into indistinguishable parts of the natural countryside should begin.

METHODOLOGY FOR DEVELOPING A
QUANTITY AND LOCATION INVENTORY
OF HAZARDOUS COMPOUNDS IN ONTARIO

P. J. Denison and K. R. Ashwood
Acres Consulting Services Limited
Niagara Falls, Ontario

INTRODUCTION

A 2-year contract was awarded in 1978 by the Air Resources Branch, Ontario Ministry of the Environment to inventory 17 specified chlorinated and aromatic hydrocarbons in Ontario. The chemical compounds of concern in this study were

Chlorinated Hydrocarbons

Carbon tetrachloride

Chloroform

Chloroprene

1,2-Dichloroethylene

Ethylene dichloride

Methyl chloride

Methylene chloride

Tetrachloroethylene

1,1,1-Trichloroethane

Trichloroethylene

Vinylidene chloride

Aromatic Hydrocarbons

Benzene

Ethylbenzene

Naphthalene

Styrene

Toluene

Xylenes

The base year for this study was 1976 since this was the most recent year that published statistics were available when the project commenced.

DATA REQUIREMENTS

The terms of reference for this study required that it be completed in two phases -

Phase A: Quantity and Location Inventory

Phase B: Emission/Discharge Inventory.

The requested information for Phase A consisted of the following for each selected chemical.

1. Company name and address
2. Plant address and industrial activity
3. Quantity in storage
4. Quantity produced/used

5. Quantity imported/exported
 - (a) from/to other provinces
 - (b) from/to other countries
6. Method of shipment (road/rail/air/sea).

For Phase B, the emission/discharge inventory, the study objectives were to obtain the following data

1. Amount released (rate)
2. Frequency (continuous/intermittent/seasonal)
3. Source of release
4. Control devices
5. For water - receiving water system
6. For soil - receiving disposal site.

A description of process operations was also required to enable comparisons to be made with published emission factors. However, it is recognized that each plant has its own unique conditions and actual data from Ontario plants were used wherever available. Releases from storage and handling facilities were also considered in this phase of the study.

DATA SOURCES

The first step in preparing this inventory was to document all potential end uses for the chemicals. This was accomplished with assistance from Corpus Information Services Ltd (chemical market consultants), and by referencing a number of organic chemistry handbooks and journal articles. Next, potential primary and secondary manufacturers, distributors and end users for the uses identified were obtained from a number of trade directories and through acquiring membership lists from these associations whose members are involved with the chemicals of concern.

Data on imports and exports were obtained from Statistics Canada and the U.S. Department of Commerce. For emissions and discharges, limited information was obtained from the U.S. Environmental Protection Agency, Environment Canada, A. D. Little Inc., GCA Corporation and Monsanto Research Corporation.

DATA GAPS

A review of the published data confirmed that much of the information was not available without making direct contact with the companies concerned. Specifically, the data gaps were as follows:

Phase A - Quantity/Location Inventory

1. Quantitative data on production, usage, storage, imports/exports
2. Method of shipment

Phase B - Emission/Discharge Inventory

1. Quantitative data on emissions/discharges
2. Site-specific data on control devices, receiving water systems, waste disposal sites.

QUESTIONNAIRE DESIGN

Separate questionnaires were designed for distribution to Ontario manufacturers and distributors, Quebec manufacturers shipping to Ontario customers, and potential Ontario users of the specified chemicals.

Information requested for each chemical included 1976 production, consumption (as a chemical intermediate and as a component in a mixture or blend), annual inventory levels, purchases from outside Ontario, and distribution within and outside Ontario. For emissions and discharges, information was requested on losses to the air, water and land including evaporative losses from storage and transfer facilities. Details on control devices and efficiencies, emission frequencies and a range of average daily emissions were also requested.

SUMMARY OF SUCCESS

Approximately 60 percent responded to the questionnaire survey. However, these responses covered 90 percent of the volumes produced or imported and subsequently used in Ontario.

It was found that 3 of the 17 hydrocarbons (chloroprene, 1, 2-dichloroethylene and vinylidene chloride) were not in commerical use in Ontario in 1976.

A review of transport modes indicated that the specified chlorinated hydrocarbons are transported primarily by road, with rail being the next most common method of shipment. The aromatic hydrocarbons studied are being transported primarily by pipeline, with rail and road being of lesser significance.

While production and consumption information from primary and secondary manufacturers could be geographically plotted accurately, a difficulty arose in plotting widespread end use for some of the specified hydrocarbons. For example, approximately 80 percent of the tetrachloroethylene produced and imported into Ontario was consumed by the dry cleaning industry in 1976. To calculate industry end usage for this chemical by city in Ontario, we determined there were 1,154 dry cleaning plants in the province from Statistics Canada and telephone directories. From a spot survey of 9 dry cleaners in Toronto, St. Catharines and Niagara Falls, an annual average of 5.6 tonnes was used. Assuming all tetrachloroethylene used by

the dry cleaning industry is eventually lost to the atmosphere, losses were plotted by multiplying 5.6 tonnes time the number of dry cleaning plants in each city.

END USE PATTERNS

Those specified chemicals with widespread usage deserve particular attention since their emissions and discharges are believed to constitute 100 percent of the amounts used.

<u>Chemical</u>	<u>Examples of Widespread Usage in Ontario</u>
Methylene chloride	paint stripper, paints, cleaning solvent
Tetrachloroethylene	dry cleaning solvent, metal degreasing, textile cleaning
1,1,1-Trichloroethane	metal cleaning, degreasing
Trichloroethylene	metal cleaning, degreasing
Toluene*	solvent in paints, resins, adhesives,
Xylenes*	rubber processing, metal cleaning, printing ink reduction, gasoline additive*

*Toluene and xylenes used as gasoline additives were quantified only as far as total amounts used in Ontario; geographical distribution in gasolines was not considered.

Based on the known amounts consumed in these widespread applications, a loss factor per capita (or per company, depending on the type of usage) was calculated to enable geographical plotting of the data.

The Ontario emission/discharge inventory covered specified chemical losses to the air, water and land during manufacture, its use as a chemical intermediate, storage and transfer, repackaging for distribution and end use. Storage and transfer losses of benzene, toluene and xylenes in gasolines were included at refinery locations; other losses of these aromatics at local filling stations or from vehicle exhausts were not included.

Bearing the above points in mind, 2 maps have been prepared showing 1976 losses of the specified chemicals in Ontario (Figures 1 and 2). While these maps show only totals for all 14 specified chemicals, detailed maps for each chemical, showing all affected Ontario locations were submitted to the Air Resources Branch, Ministry of the Environment.

In conclusion, based on the 1976 results obtained, there is no indication that emissions and discharges of the specified chemicals approach current preliminary estimates of hazard levels outlined in MOE guidelines and standards. However, due to the limited amount of ambient air quality data available, it has been recommended that additional quantitative information be collected to enable a more accurate assessment of the situation. This may become critical in

view of the controversy centered around many of these chemicals suspected of being human carcinogens. Also, we are not yet fully cognizant of the effects of chemical interactions which can be independent, additive, synergistic or antagonistic (i.e. the effect of one chemical reduces the effect of another chemical). Until more scientific evidence is available, it is necessary to take a cautious approach by compiling inventories of suspect chemicals. In this way, if and when action is required, the Ministry has the capability to proceed without delay.

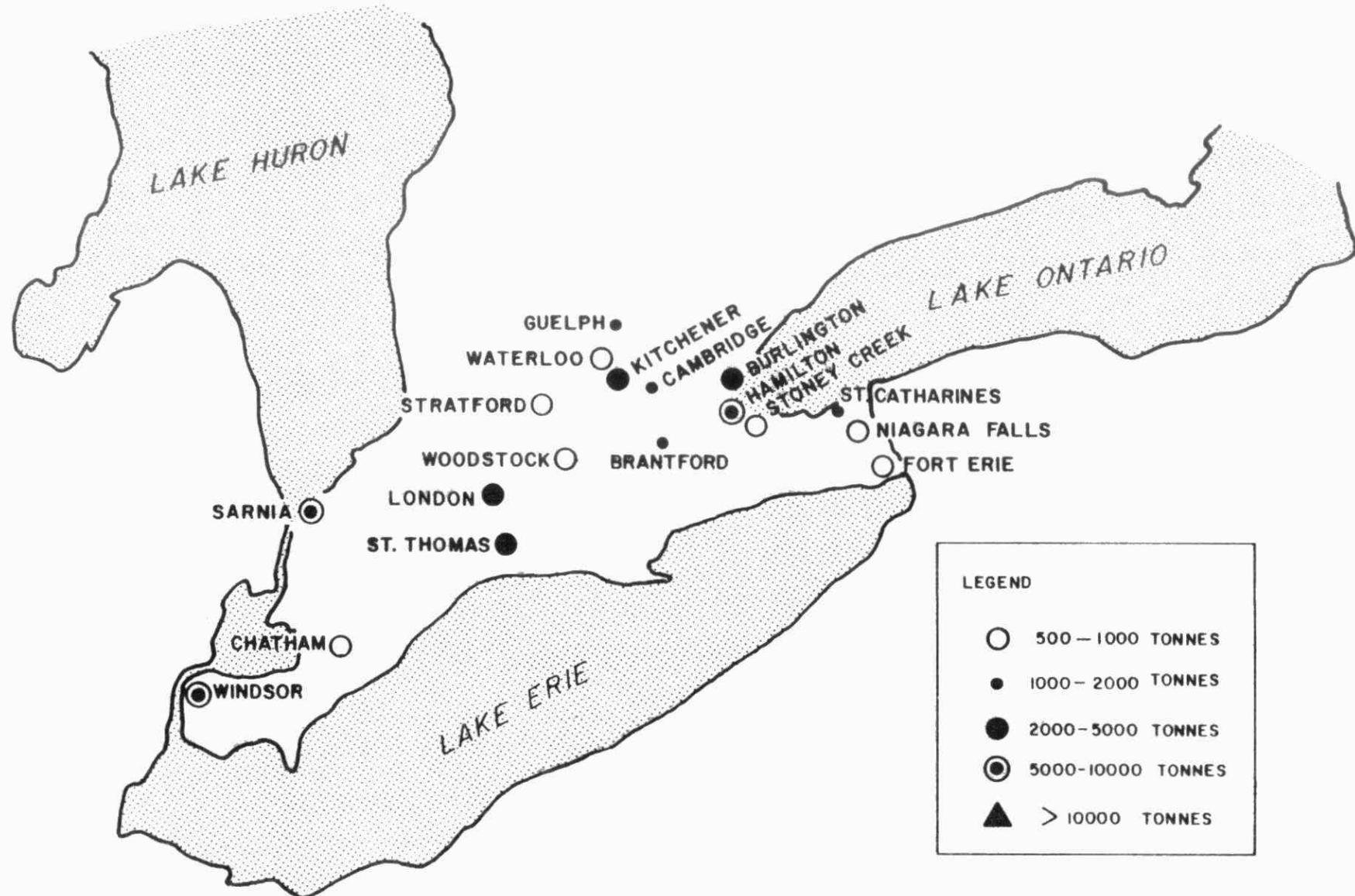


FIGURE 1—SAMPLE DISTRIBUTION OF EMISSIONS & DISCHARGES
FOR 14 SPECIFIED CHLORINATED & AROMATIC
HYDROCARBONS IN SOUTHWESTERN ONTARIO

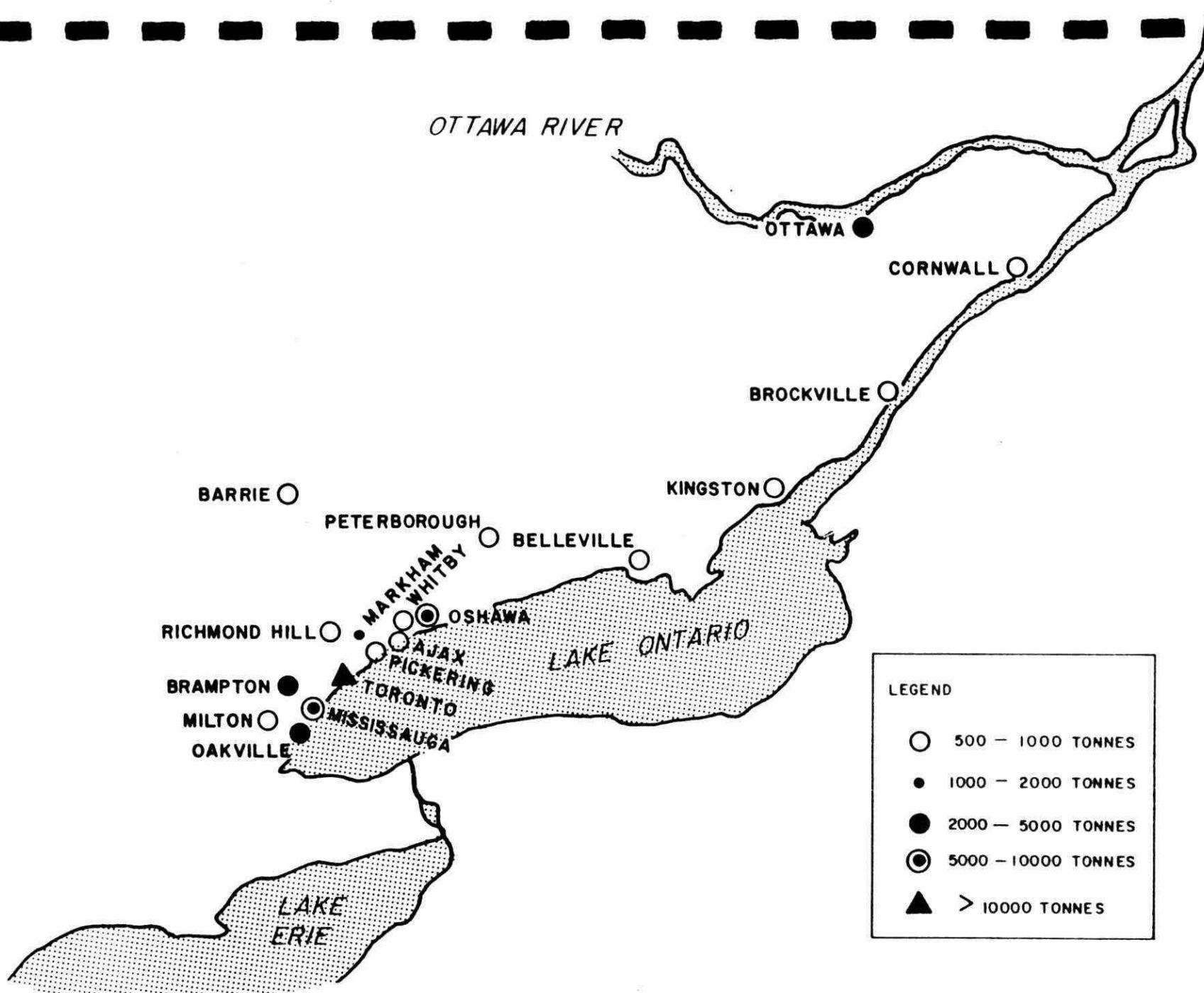


FIGURE 2-SAMPLE DISTRIBUTION OF EMISSIONS & DISCHARGES
FOR 14 SPECIFIED CHLORINATED & AROMATIC
HYDROCARBONS IN SOUTHEASTERN ONTARIO

ONTARIO'S SEVEN POINT PROGRAM FOR LIQUID INDUSTRIAL WASTE DISPOSAL

Ministry of the Environment
Liquid and Special Industrial
Waste Management Program

1. FACILITIES

- WORK WITH PRIVATE SECTOR
- LONG-TERM WASTE MANAGEMENT PLAN
- ACQUISITION OF SITES

2. INTERIM MEASURES

- GUIDELINES
 - TREATMENT AND DISPOSAL
 - LANDFILL PROHIBITION
 - MONITORING AND CONTROL
- WASTE STORAGE
 - PCB
 - OTHER WASTES

3. WAY-BILL MONITORING

- EDP SYSTEM

4. WASTE CLASSIFICATION

5. REGULATIONS

- LANDFILL PROHIBITION
- TREATMENT AND DISPOSAL
- REGISTRATION OF WASTES

6. PERPETUAL CARE

- STUDY
- REGULATIONS

7. TRANSBOUNDARY MOVEMENT OF WASTES

FACILITIES FOR LIQUID INDUSTRIAL WASTE TREATMENT AND DISPOSAL

A) GOVERNMENT

MacLAREN STUDY

- LONG-TERM WASTE MANAGEMENT PLAN
- FIVE YEARS TO DEVELOP AND IMPLEMENT(?)

B) PRIVATE SECTOR

REGION OF DURHAM PROPOSAL TO CONVERT THE AJAX STP INTO PHYSICAL/CHEMICAL TREATMENT FACILITY

- ENVIRONMENTAL HEARING UNDER THE
ENVIRONMENTAL PROTECTION ACT COMMENCED
DECEMBER 17, 1979. DUE TO BE COMPLETED
JUNE 20, 1980,

c) PCBs

1. MacLAREN STUDY TO INCORPORATE NEED FOR
PCB DESTRUCTION FACILITIES
2. ST. LAWRENCE CEMENT KILN
 - TEST BURN
 - CITY OF MISSISSAUGA BY-LAW

INTERIM MEASURES

1. LIQUID INDUSTRIAL WASTES

- A) IMPROVED MONITORING AND CONTROLS ON 22
LANDFILL SITES CURRENTLY ACCEPTING LIQUIDS
- B) LIMITED-TERM (FIVE YEARS) SOLIDIFICATION
PROPOSALS
 - BROWNING-FERRIS INDUSTRIES LIMITED
AT RIDGE LANDFILL SITE IN TOWNSHIP
OF HARWICH
 - WALKER BROTHERS QUARRIES LIMITED AT
QUARRY SITE IN ST. CATHARINES AREA
 - PROPOSALS SUBJECT TO THE ENVIRONMENTAL
ASSESSMENT ACT
 - MINISTRY OF THE ENVIRONMENT CO-PROONENT
 - DOCUMENTS FILED WITH MINISTER ON MAY 9, 1980.
 - HEARING IN LATE FALL?

INTERIM MEASURES

2. PCBs

A) M. M. DILLON STUDY ON INTERIM STORAGE OF PCBs

- REVIEW OF CROWN LANDS (AND OTHERS) IN PROVINCE
- THREE PREFERRED SITES
 - ONTARIO HYDRO TRANSFORMER STATION IN MIDDLEPORT
 - CAYUGA PROPERTIES
 - RIDGE LANDFILL (BFI)
- MINISTRY ELECTED TO PROCEED WITH MIDDLEPORT:
 - GOVERNMENT OWNED LAND;
 - CLOSE TO CENTROID OF WASTE PCB GENERATION;
 - REASONABLE ROAD ACCESS;
 - NOT CLOSE TO URBAN AREA
- SUBJECT TO ENVIRONMENTAL ASSESSMENT ACT
- CONSULTANT PRESENTLY PREPARING ASSESSMENT DOCUMENTS (6 MONTHS)

B) REGULATION ON MOVEMENT OF PCBs

(TO BE DEALT WITH LATER)

WAY-BILL MONITORING PROGRAM

- NEW WAY-BILL INTRODUCED IN JANUARY, 1979, PROVING TO BE A DEFINITE IMPROVEMENT
- STUDY COMPLETED ON OPTIMAL APPROACH TO HANDLING WAY-BILLS AND PROCESSING DATA
- AN 'INTELLIGENT TERMINAL' LOCATED IN WASTE MANAGEMENT BRANCH WILL BE USED TO INPUT DATA AND PRODUCE MINOR REPORTS. THIS WILL BE SUPPORTED BY THE GOVERNMENT MAIN COMPUTER FOR THE PRODUCTION OF MAJOR REPORTS AND STATISTICS.
- NEW SYSTEM TO BE IN PLACE THIS YEAR SUBJECT TO EQUIPMENT DELIVERY



Ministry
of the
Environment
Ontario

Transfers of Liquid Industrial Waste

Ontario Regulation 926/76

C 99883

Important: See Instructions on Reverse

SOURCE (Complete Section A Only. Please Print)

Company Name				
Waste Source Location _____				
City/Town _____				
Waste Description: Check One				
101 <input type="checkbox"/> Acids	201 <input type="checkbox"/> Oily Water	301 <input type="checkbox"/> Pigments, Paint, Printing & Adhesives		
102 <input type="checkbox"/> Alkalies	202 <input type="checkbox"/> Waste Oils	302 <input type="checkbox"/> Pesticides		
103 <input type="checkbox"/> Metal Finishing Wastes	203 <input type="checkbox"/> Organic Solvents	303 <input type="checkbox"/> Detergents, Cleaners & Soaps		
104 <input type="checkbox"/> Cyanides	204 <input type="checkbox"/> Chlorinated Solvents	304 <input type="checkbox"/> Pharmaceutical & Cosmetics		
105 <input type="checkbox"/> Chemical Fertilizer Wastes	205 <input type="checkbox"/> Plastic Resins	401 <input type="checkbox"/> Plant & Animal Wastes		
106 <input type="checkbox"/> Phosphates	206 <input type="checkbox"/> Amines	402 <input type="checkbox"/> Inert Sludges		
107 <input type="checkbox"/> Other Inorganic	207 <input type="checkbox"/> Glycerin			
	208 <input type="checkbox"/> Phenols			
	209 <input type="checkbox"/> PCB's			
190 <input type="checkbox"/> Other	290 <input type="checkbox"/> Other			
(Specify)	(Specify)			
Quantity	_____ □ Gallons □ Litres			
Time	Day	Month	Year	Signature of Authorized Person
Released				

RECEIVER (Complete Section B Only. Please Print)

Company Name		MOE Certificate of Approval No.		
Site Location _____		A <input type="checkbox"/> _____		
City/Town _____				
Transfer		Final <input type="checkbox"/> Secure Landfill		
To:		or Disposal <input type="checkbox"/> Incineration		
<input type="checkbox"/> _____		by <input type="checkbox"/> Other (State Method)		
Time	Day	Month	Year	Signature of Authorized Person
Received				

CARRIER (Complete Section C Only. Please Print)

Company Name		Waste Manifest System Number								
Address _____ Number _____ Street _____		A <input type="checkbox"/> _____								
City/Town _____										
Vehicle License Plate Number _____		Signature of Driver _____								
<table border="1"> <tr> <td>-</td> <td> </td> </tr> </table>		-								
-										

MOE 1270 (7/79)

MINISTRY COPY

QUANTITIES OF LIQUID INDUSTRIAL WASTES GENERATED IN ONTARIO
 (SUMMARY REPORT) JANUARY TO DECEMBER, 1979

WASTE CLASSIFICATION	VOLUME (GALLONS)
101 ACIDS	4,060,100
102 ALKALIS	1,746,000
103 METAL FINISHING WASTES	2,847,400
104 CYANIDES	41,700
105 CHEMICAL FERTILIZER WASTES	641,100
106 PHOSPHATES	262,000
190 OTHER (INORGANIC)	7,076,600
201 OILY WATER	14,542,000
202 WASTE OILS	2,477,800
203 ORGANIC SOLVENTS	2,839,200
204 CHLORINATED SOLVENTS	95,800
205 PLASTIC RESINS	1,094,900
206 AMINES	279,200
207 GLYCOLS	421,600
208 PHENOLS	503,700
209 PCB's	14,600
290 OTHER (ORGANIC)	3,991,000
301 PIGMENTS, PAINT, PRINTING AND ADHESIVES	3,184,300
302 PESTICIDES	216,000
303 DETERGENTS, CLEANERS AND SOAPS	402,000
304 PHARMACEUTICAL AND COSMETICS	22,000
401 PLANT AND ANIMAL WASTES	2,819,200
402 INERT SLUDGES	11,094,900
UNSPECIFIED	874,000
GRAND TOTAL	61,547,100

LIQUID INDUSTRIAL WASTES

DISPOSAL METHODS

1979

VOLUME
(MILLIONS OF GALLONS)

INCINERATION 19.0

LANDFILL 36.0

EXPORT 5.0

MISCELLANEOUS 1.5

TOTAL 61.5

REGULATIONS AND GUIDELINES

1. REGULATIONS

- a) MOVEMENT OF EQUIPMENT CONTAINING PCBs
 - DRAFT COMPLETED AND APPROVED, WAITING FOR ADMINISTRATIVE GUIDELINES.
- b) REGISTRATION OF WASTES
 - STUDY COMPLETED OF APPROACH IN OTHER JURISDICTIONS THROUGHOUT WORLD
 - REGULATIONS EXPECTED TO BE DRAFTED BY END OF YEAR
- c) PROHIBITION ON LANDFILLING OF LIQUID WASTES
 - REGULATION IN ABEYANCE PENDING AVAILABILITY OF ALTERNATIVE TREATMENT AND DISPOSAL FACILITIES

2. GUIDELINES

- a) POLLUTION PREVENTION AND WASTE MANAGEMENT GUIDELINES FOR PCBs, NOVEMBER, 1978, TO BE REVISED.
- b) WASTE CLASSIFICATION GUIDELINES TO BE REVISED CONSISTENT WITH REGISTRATION OF WASTE REGULATION
- c) TREATMENT AND DISPOSAL OF LIQUID INDUSTRIAL WASTE GUIDELINE TO BE UPDATED OR CONVERTED INTO REGULATION
- d) WASTE OIL GUIDELINE TO BE REVISED PENDING POLICY ON ROAD OILING

PERPETUAL CARE PROGRAM

- TASK FORCE ESTABLISHED EARLY IN 1979
- TERMS OF REFERENCE TO ENSURE SOURCE OF FUNDING FOR SHORT-TERM AND LONG-TERM (AFTER CLOSURE) CONTINGENCIES AT LANDFILL SITES
- CONCLUDED THAT MEASURES REQUIRED IN:
 - a) OPERATIONAL SECTOR DURING OPERATION AND CLOSURE AND FOR SUBSEQUENT MONITORING AND MAINTENANCE
 - b) LIABILITY INSURANCE - OFF-SITE PROTECTION FOR THIRD PARTIES
 - c) CARE IN PERPETUITY - TO PROVIDE LONG-TERM MAINTENANCE AND PROTECTION AND FOR CONTINGENCIES NOT COVERED BY OTHER MEASURES.
- WORK WAS DELAYED PENDING REPORT FROM CONSULTANT ON AVAILABILITY OF INSURANCE.
- DETAILS NOW TO BE RESOLVED:
 - a) HOW CAN OWNERS OF SITES BE REQUIRED TO SECURE THE NECESSARY FUNDING?
 - b) WHAT IS REASONABLE LEVEL OF INSURANCE?
 - c) WHAT ARE REASONABLE SURCHARGES FOR THE ESTABLISHMENT OF PERPETUAL CARE FUND?
- REPORT EXPECTED TO BE FINALIZED BY END OF YEAR.

THE HONOURABLE HARRY C. PARROTT, D.D.S.
MINISTER OF THE ENVIRONMENT

STATEMENT TO THE LEGISLATURE

RE: ONTARIO WASTE MANAGEMENT CORP.
(STATEMENT OF POLICY)

QUEEN'S PARK, TORONTO
NOVEMBER 25, 1980

MR. SPEAKER:

As I indicated in the House two weeks ago, I have received the MacLaren Report which recommends options on permanent liquid waste treatment facilities. I have had an opportunity to thoroughly examine the recommendations and I would like to table it at this time. The appendices to this report will be tabled as soon as they are printed.

As the Members will remember, I referred the issue of liquid industrial waste to the Standing Committee on Resources Development in November 1978. As a basis for discussion, I put forward a seven-point program which represented our plan of attack on the liquid waste problem.

After an intensive review of our proposals and the problem it would address, the Committee submitted its report. At this time, I would like to remind the Members once again how closely we have taken their advice in implementing our seven-point program.

There were 47 different recommendations and suggestions in that report. A total of 38 have either been completely implemented or are in the planning stages. The rest are under active consideration. /

OBVIOUSLY, THE COMMITTEE'S REPORT WAS OF GREAT ASSISTANCE TO US.

THERE WERE FIVE SPECIFIC OPTIONS PROPOSED FOR ESTABLISHING FACILITIES. IN THE INITIAL STAGE OF OUR PLAN FOR SHORT TERM FACILITIES, WE ACCEPTED THEIR THIRD OPTION -- JOINT PUBLIC-PRIVATE OWNERSHIP OF SITES AND FACILITIES. WE ACCEPTED THE COMMITTEE'S VIEW THAT WE ASSIST COMPANIES TO ESTABLISH NEW TECHNOLOGY.

WE HAVE ACCEPTED THEIR VIEWS AND YET IT IS WITH CONCERN AND REGRET THAT I FIND DELIBERATE ATTEMPTS TO HALT IMPLEMENTATION OF THOSE OPTIONS.

I NEED NOT OUTLINE THE LITANY OF EVENTS WHICH HAVE FRUSTRATED OUR EFFORTS TO PROCEED WITH RATIONAL HEARINGS. CERTAIN ACTIONS HAVE ONLY INTENSIFIED THE PUBLIC'S FOCUS ON THE "NOT IN MY BACKYARD" SYNDROME. LOST IN THAT APPROACH IS THE VERY CRUCIAL ARGUMENT THAT THE TREATMENT PROPOSED IS THE ONLY WAY TO GUARANTEE THE SAFETY THEY SO EARNESTLY DESIRE.

MR. SPEAKER, IT IS OBVIOUS THE AMAZINGLY CONSISTENT RESPONSE WE HAVE RECEIVED IN EVERY LOCATION, AND EXPERIENCE THROUGHOUT NORTH AMERICA DEMONSTRATES/THAT WE ARE ENCOUNTERING A KIND OF SOCIAL PHENOMENA.

MY ONE GOAL IS TO STOP THE LANDFILLING OF UNTREATED LIQUID WASTE. THAT IS NOT ONLY A STRONG COMMITMENT FROM ME, BUT OF THIS GOVERNMENT.

BUT QUITE FRANKLY, THE CONTROVERSY SURROUNDING EACH PROPOSAL HAS MEANT THAT IT HAS TAKEN TOO LONG TO IMPLEMENT WHAT I'M SURE EVERYONE AGREES IS A LEGITIMATE OBJECTIVE. HOWEVER, THAT INTERVAL HAS BEEN USED PRODUCTIVELY.

THERE HAS BEEN TIME FOR THE COMPLETION OF THE MACLAREN REPORT. AND IT CLEARLY INDICATES THE PRESSING NEED FOR AN IMMEDIATE SOLUTION.

TWO WEEKS AGO, I ANNOUNCED A FREEZE ON MINISTRY ACTIVITIES AND PARTICIPATION IN OUR SHORT TERM PROPOSALS. I WANTED TIME TO ASSESS OUR OTHER OPTIONS AND TO WEIGH MACLAREN'S RECOMMENDATIONS. IN REACHING TODAY'S DECISION I RELIED HEAVILY ON THE STANDING COMMITTEE'S OPTION OF GOVERNMENT OWNERSHIP AND CONTROL AS WELL AS THE MACLAREN REPORT.

IN THEIR FIRST REPORT, MACLAREN OUTLINED BASIC CRITERIA FOR ASSESSMENT OF SITES. IT WAS APPARENT THERE WOULD BE EXTREME DIFFICULTY IN OBTAINING ONE SITE TO MEET ALL CRITERIA.

ONE MACLAREN ENGINEER SAID: "UNDER THE CRITERIA AGREED ON, WE ELIMINATED ALL AREAS IN SOUTHERN ONTARIO WITHIN FIVE MILES OF ANY CITY, TOWN OR VILLAGE. PROVINCIAL AND FEDERAL PARK, ALL INDIAN RESERVATIONS, CONSERVATION AUTHORITY LAND, FLOOD LAND, ECOLOGICALLY SENSITIVE LAND AND CLASS 1 OR CLASS 2 AGRICULTURAL LAND. WHEN WE GOT THROUGH, THERE WASN'T MUCH OF THE PROVINCE LEFT!"

IN EARLY JUNE I REQUESTED MACLAREN ASSESS TWO ADDITIONAL SITES -- CROWN LAND IN SOUTH CAYUGA AREA AND LAND AT CAMP BORDEN, PREVIOUSLY SUGGESTED BY THE FEDERAL DEPARTMENT OF THE ENVIRONMENT.

BESIDES A LACK OF SUITABLE SITES, IT WAS CLEAR THAT THE PUBLIC, AS WELL AS MEMBERS OF THE HOUSE, FEEL THAT ONLY GOVERNMENT CONTROL AND OWNERSHIP WILL GUARANTEE THE SAFETY OF THOSE FACILITIES.

TODAY'S REPORT RECOMMENDS THE PROVINCE ACQUIRE ONE OR MORE SITES ON WHICH IT WOULD BE POSSIBLE TO CONSTRUCT WASTE MANAGEMENT FACILITIES. IT CONCLUDES THAT LAND IN SOUTH CAYUGA AND FIVE OTHER AREAS HAS POTENTIAL FOR SUCH A SITE -- HURON COUNTY, LAMBTON COUNTY, BRUCE COUNTY AND TWO LOCATIONS IN SIMCOE COUNTY.

THE TWO SITES PREFERRED BY MACLAREN ARE THE ONE IN HURON AND THE ONE IN THE SOUTH CAYUGA AREA. BOTH ARE CONSIDERED "VIABLE LOCATIONS FOR THE PROPOSED FACILITIES SUBJECT TO THEIR GEOLOGICAL SUITABILITY BEING CONFIRMED BY FIELD STUDIES."

MACLAREN STATES CAYUGA OFFERS AN ADDITIONAL ADVANTAGE BECAUSE IT IS CLOSE TO WASTE GENERATORS. I BELIEVE THE FACT THAT THE GOVERNMENT ALREADY OWNS MUCH OF THE LAND IS ANOTHER MAJOR PLUS. THIS ALLOWS ADEQUATE GOVERNMENT CONTROL OF THE SITE; A BUFFER ZONE CAN EASILY BE ACHIEVED; AND THERE WILL BE MINIMAL DISRUPTION IN TERMS OF EXISTING LAND USE AND TO ANY RESIDENTS. THE ASSEMBLY OF PRIVATELY OWNED LAND IN THE OTHER AREAS WOULD RESULT IN MASSIVE EXPROPRIATION AND CONSIDERABLE COST TO OBTAIN THE NEEDED PROPERTIES.

BEFORE A DECISION COULD BE MADE, WE CARRIED OUT SOIL TESTS IN CAYUGA. THE ENGINEERING FIRM OF MORRISON BEATTY LIMITED WAS RETAINED. THEIR REPORT STATES "THE SITE APPEARS TO BE IDEALLY SUITED" FOR WHAT WE PROPOSE.

BASED ON THESE FACTORS, I HAVE DECIDED THAT LAND IN THE SOUTH CAYUGA AREA WILL BECOME THE PROVINCE'S PERMANENT LIQUID INDUSTRIAL WASTE TREATMENT FACILITY. IT WILL HAVE THE BEST AVAILABLE TECHNOLOGY AND OPERATE UNDER THE HIGHEST STANDARDS.

ONE IMPORTANT ASPECT OF THE GOVERNMENT OWNERSHIP MEANS WE CAN AND DO FULLY ACCEPT THE RESPONSIBILITY AS A GOVERNMENT FOR THE OPERATION OF SUCH A SITE.

THE SITE WILL BE RUN BY A NEWLY FORMED CORPORATION WITH A BOARD OF DIRECTORS OF TWO REPRESENTATIVES FROM THE GENERAL PUBLIC, TWO MEMBERS OF THE LOCAL COMMUNITY, TWO TECHNICAL EXPERTS AND A CHAIRMAN APPOINTED BY THE GOVERNMENT. THEY WILL BE RESPONSIBLE FOR OVERSEEING DEVELOPMENT OF THE FACILITY.

CALLED THE ONTARIO WASTE MANAGEMENT CORPORATION, THIS COMPANY WILL BE INCORPORATED IMMEDIATELY. I WILL SHORTLY INTRODUCE LEGISLATION TO SET UP A CROWN CORPORATION TO ASSUME MANAGEMENT AND DEVELOPMENT RESPONSIBILITIES.

TO HANDLE SHORT TERM NEEDS, CONSTRUCTION WILL BEGIN AS SOON AS POSSIBLE ON THE SECURE LANDFILL SITE, A SOLIDIFICATION PLANT, A COMPLETE LAB AND SPECIAL STORAGE FACILITIES. THE SITE WILL ULTIMATELY CONTAIN AN INCINERATION UNIT AND OTHER TREATMENT FACILITIES.

I ACCEPT THE MACLAREN RECOMMENDATION THAT THE SITE ITSELF WILL BE 100 ACRES IN SIZE WITH A BUFFER ZONE OF 640 ACRES. ADDITIONALLY, WE ARE DEVELOPING A FURTHER CONTROL ZONE OF APPROXIMATELY ONE MILE ON ALL SIDES FROM THE BOUNDARIES OF THE FACILITY.

WITHIN THE BUFFER ZONE AROUND THE SITE NO RESIDENTS WILL BE PERMITTED. IN THE OUTER CONTROL ZONE WE WILL WELCOME FARMING ON A LEASE-BACK BASIS TO DEMONSTRATE THE SUITABLE CO-EXISTENCE OF THE SITE AND THE NORMAL ACTIVITY FOR THE AREA.

I HAVE ADVISED THE CO-PROPOONENTS AT THOROLD AND HARWICH THAT WE ARE WITHDRAWING OUR PARTICIPATION FROM THE SHORT TERM PROPOSALS. THIS NEW SITE WILL REPLACE THE INTERIM STORAGE PROPOSAL FOR PCBs IN MIDDLEPORT AS WELL. WE ARE OF COURSE PREPARED TO MEET ALL OUR LEGAL OBLIGATIONS.

THE SOUTH CAYUGA SITE WILL BE DESIGNED TO HANDLE THE BULK OF ONTARIO'S LIQUID WASTE.

OTHER POINTS ON THIS NEW FACILITY:

1. THE WASTE MANAGEMENT CORPORATION WILL ASSIST AND SUPERVISE ROUND-THE-CLOCK SECURITY.
2. WITH THE LAB FACILITIES IN PLACE, NO WASTES WILL EVER ENTER THAT SITE BEFORE THE CONTENTS ARE FULLY KNOWN.
3. THERE WILL BE NO RADIOACTIVE MATERIAL ACCEPTED.
4. THE PROVINCE WILL ASSUME COST OF UPGRADING AND/OR CONSTRUCTION OF THE NECESSARY ROADS TO REDUCE TRANSPORTATION RISKS TO THE ABSOLUTE MINIMUM.
5. THE MINISTRY OF THE ENVIRONMENT WILL CONTINUE TO FUND RESEARCH INTO ALTERNATIVE TECHNOLOGIES. THESE TO BE INCORPORATED WITHIN SITE WHERE APPROPRIATE.
6. THE SITE WILL BE OPERATED ON A BREAK-EVEN BASIS. THE USER FEES WILL ACT AS AN INCENTIVE TO ENCOURAGE INDUSTRY TO REDUCE, RECYCLE OR RE-USE THEIR WASTES. THE BOARD WILL ALSO INVESTIGATE OTHER WAYS TO REDUCE WASTE VOLUMES AND ENCOURAGE WASTE EXCHANGE PROGRAMS.

MR. SPEAKER, LET THERE BE NO DOUBT OF THE URGENT NEED FOR THIS FACILITY. OUR HEALTH AND THAT OF THE ENVIRONMENT DEPEND ON IT. BECAUSE OF THAT NEED, I HAVE COME TO ANOTHER DIFFICULT DECISION.

SINCE THE FINAL DECISION ON SITE LOCATION AND INITIAL SOLIDIFICATION TECHNOLOGY IS MADE, NO HEARING WILL BE HELD UNDER THE ENVIRONMENTAL ASSESSMENT ACT OR THE EXPROPRIATIONS ACT ON THE FEW PROPERTIES THE GOVERNMENT DOES NOT YET OWN.

MUCH WORK MUST STILL BE DONE TO DEVELOP THIS FACILITY. BUT I FELT IT NECESSARY TO INFORM THE PUBLIC AS SOON AS IT WAS POSSIBLE TO DO SO.

MR. SPEAKER, THE COST OF THIS FACILITY IS ESTIMATED AT APPROXIMATELY \$60 MILLION. THAT IS CERTAINLY HIGH BUT THE GOVERNMENT FEELS THAT COST SHOULD NOT BE THE LIMITING FACTOR WHEN WHAT WE NEED IS THE BEST TECHNOLOGY IT IS POSSIBLE TO ESTABLISH.

WE ARE NOT ABLE TO LOOK TO OTHER JURISDICTIONS IN CANADA FOR ANY GUIDANCE WHATSOEVER. HOWEVER, AS SOON AS THE BOARD IS IN PLACE, I INTEND TO TOUR FACILITIES IN EUROPE WITH THEM SO THAT THEY CAN COPY OR IMPROVE WHERE APPROPRIATE, THE LATEST IN WASTE TREATMENT TECHNOLOGY, SO THAT WE MAY HAVE THE BEST FACILITY IN THE WORLD.

IT IS WITH SOME PRIDE THAT I NOTE THE LEADERSHIP ROLE
ONTARIO IS TAKING IN TACKLING THIS SERIOUS ISSUE. AND I
FULLY INTEND TO KEEP IT THAT WAY.

Environmental Impairment Liability Insurance
by
G.T.G. Scott, Consulting Engineer

The purpose of this paper is to report on a study undertaken for the Ontario Ministry of the Environment during 1979 covering the possible availability and use of Environmental Impairment Liability Insurance to cover exposures associated with the operation of waste disposal systems and facilities. However, Environmental Impairment Liability Insurance being a relatively new type of cover with which many people are probably unfamiliar, it would appear appropriate to explain what this insurance is and what cover it provides before going into details of the actual study involved.

Prudent management dictates that where an individual or organization is, in the course of their activities, exposed to a risk, then provisions should be made to ensure that funds are available to cover claims resulting from that risk or exposure. While larger organizations may provide reserve funds for such contingencies, or self insure, it is common practice to carry Comprehensive General Liability Insurance to cover the wide variety of risks to which businesses are exposed. Historically such Comprehensive General Liability Policies contained no Environmental exclusion. In other words these policies covered the insureds liability for environmental damage resulting from their operations.

In recent years public awareness of the aesthetic and material damage resulting from discharges of materials to the environment, and claims for such damages, have increased in both frequency and magnitude. At the same time courts of law have progressively eased the path of the plaintiff attempting to obtain redress for damages whether real or imaginary. It is hardly surprising that insurers, faced with this situation, reacted in various ways to protect their interests.

While marine risks are not the subject of this presentation it is probably worth noting the reaction in that area that followed such incidents as that of the tanker the Torrey Canyon. Tanker owners took the initiative under the TOVALOP Agreement by voluntarily accepting

liability for coastal pollution arising from a tanker mishap. They have provided, with the assistance of insurers, the necessary financial guarantee for claims and clean-up costs. Similar agreements were subsequently made under OPOL for offshore oil operations. Thus, insurance cover for environmental impairment has been made available to shipowners, charterers, salvors and offshore oil operators.

However, for the land based risks which are the subject of our current discussions the approach taken by insurers has been much more restricted. In general terms, while cover has been made available for environmental impairment liability resulting from an accident, or sudden, unexpected and unintended happening, there has been a virtually unanimous refusal to accept similar exposures from "steady state" operations. In other words, while coverage for environmental damage resulting from "acute" conditions may be provided under a comprehensive general liability policy, damage resulting from "chronic" conditions is invariably excluded.

While the attitude adopted by insurers towards landbased environmental impairment liability risks, as described above, may appear to be harsh, it is perhaps not unreasonable when one considers the loss experience during recent years and the posture adopted by courts of law that has eased the path of plaintiffs.

Fortunately, for those individuals or organizations whose activities, by their very nature, present an exposure to potential claims for environmental damage, the need for appropriate insurance cover was recognized by a group of European re-insurance companies. As a result of a meeting held in Paris in 1972, a plan for "total pollution cover" was developed and is now available worldwide to cover the legal liability arising from any form of environmental impairment, whether sudden and accidental or not. This coverage has been named "Environmental Impairment Liability Insurance."

One might well query why the name environmental impairment was favoured for this insurance, rather than the shorter form "pollution". An examination of the definition of environmental impairment, as contained in the policy wording provides good reasons for the use of this term.

The policy states as follows:- "for the purpose of this policy, environmental impairment is defined as:-

- a) the emission, discharge, dispersal, disposal, seepage, release or escape of any liquid, solid, gaseous or thermal irritant, contaminant or pollutant into or upon land, the atmosphere or any water course or body of water.
- b) The generation of smell, noises, vibrations, light, electricity, radiation, changes in temperature or any other sensory phenomena arising out of or in the course of the insured's operations, installations or premises all as designated in the schedule."

From the above, it should be obvious that the plan does indeed provide for "total pollution cover".

It should be noted that the policy avoids the term "occurrence" and that the insurers will indemnify on a "claims made" basis. A claim is defined as "any single claim or series of claims resulting from one and the same isolated, repeated or continuing environmental impairment."

The same comprehensive approach has been followed in defining the indemnifiable effects of environmental impairment. Cover applies to claims, not only for personal injury (including death at any time resulting therefrom) and for property damage, but also for "impairment or diminution of, or other interference with any other right or amenity protected by law." The need for this extension becomes apparent when one considers the potential for environmental suits brought for unusual reasons, such as the destruction of a scenic view, the obstruction of TV reception by a highrise building, the hampering of birdwatching by smog, or the impairment of recreational facilities by smelly or murky effluent.

In addition to the compensation payments for damages, the policy also indemnifies for clean up costs incurred whether necessary as a result of legal obligation or to prevent an insured loss, and also pays for costs and expenses of litigation.

As with any insurance cover, there are exclusions to this policy, which

fall under two specific headings.

The first type of exclusion includes those which are absolute such as consequences of war risks, nuclear risks and claims from the insured's employees. An absolute exclusion also applies to fines, penalties and punitive damages.

There is also an exclusion which deals with intentional acts. This exclusion has been carefully worded so that it applies where an executive director or any officer of the insured or any employee with specific responsibility for environmental control, is aware of non-compliance with any applicable regulation or instruction related to environmental impairment, issued by a competent authority. However, the cover does remain in force if the insured is operating under conditions of non-compliance with the consent of the jurisdictional authority and with the intent to comply as soon as can reasonably be expected. In a way this is a good faith clause with the insured and the insurer working together.

Further exclusions are inserted in the policy on a optional "buyback principle". These include environmental impairment involving a sudden, unintended and unexpected happening; vehicles; water craft; oil or gas drilling platforms; deep water ports; aircraft or airport operation; product liability; genetic damage; damage to the insured's property or property in his care, custody or control; and joint liability with others. Under appropriate circumstances it may be possible to amend or delete one of more of these exclusions when coverage is not otherwise available to the insured. So far as sudden, unintended and unexpected happenings are concerned, for most insureds, these events are covered under their CGL policies and the exclusion only operates to prevent overlapping coverage. However, some insureds, especially those utilising certain hazardous operations, may no longer be provided this coverage under their CGL policy. For those firms, EIL insurance provides valuable protection.

Since actuarial information relating to environmental impairment liability claims is still virtually nonexistent, risks are rated by reference to a rating manual based on an analytical approach. In addi-

tion to quantifying what might be called the static risk elements, by reference to this rating manual, there are a number of variable factors which insurers must take into account when rating any individual operation. These include the size of the insured's business, the extent of pollution already present in the surrounding environment, methods employed for waste disposal, past record of claims, degree of risk awareness on the part of plant management and staff, and the quality of internal housekeeping. Also to be numbered among the variable factors are the strictness of standards laid down by authority for the industry or area concerned, the relative effectiveness of enforcement agencies, the type of liability imposed by statute and the practice of the courts relating thereto.

Each risk is therefore the subject of a technical assessment or survey by independent scientific consultants. While the survey is commissioned by the insured, a portion of the first years premium is rebated to the insured to assist in paying all or part of the cost of this report if environmental impairment cover is subsequently purchased.

With this background as to the nature and operation of the Environmental Impairment Insurance program, the project undertaken for the Ontario Ministry of the Environment can be reviewed in a clearer light.

The purpose of the project was to examine the availability of this insurance to cover certain aspects of the operations of waste management systems and waste disposal operations and to ascertain the terms under which the insurance would be made available. In addition preliminary cost estimates were obtained based on two specific waste disposal operations in the Province. Reference was made during the course of the study to the Interim Report on Perpetual Care for Waste Management Facilities prepared by the Perpetual Care Task Force of the Ministry of the Environment. This document sets out the type and extent of liability insurance which may be required to provide off-site protection for third parties.

Discussions were held with representatives of the managers of the insurance program, H. Clarkson (Overseas) Limited in London, England,

from which it was established that Environmental Impairment Liability Insurance as described above is in fact available to provide the liability cover under consideration. Such cover is available to the owners, operators and users of waste management systems and waste disposal sites, as a means to ensure that such parties are in a position to meet their financial obligations in the event that claims are made by third parties whose interests are damaged by the operations involved.

Of particular interest was the reaction of the insurers to the request for similar cover for operations involving the handling, treating and otherwise disposing of liquid, hazardous, hospital and other similar types of waste which might be considered "special" in nature or presenting "unusual" environmental hazards. There again the response was positive, although the provision of insurance for such facilities will be considered on a case by case basis.

Non-binding "Premium Indications" and details of applicable limits and deductibles are readily available from the insurers through Canadian Insurance Brokers on submission of certain basic information. This information comprises details of the owner or operator of the facility, its location and history, the processes and operations involved, data concerning compliance with regulatory requirements and of course particulars of any incidents or claims that have occurred involving environmental impairment. Where available or applicable financial information is also required together with details of other liability insurance coverage carried. These Premium Indications are non-binding, are normally valid for a period of six months, and are subject to the preparation of the technical evaluation referred to above.

Subsequent to the receipt by the insured of the technical evaluation known as an Environmental Risks Analysis Report, a firm "Premium Quotation" is provided by the Insurers.

The general form and provisions of the cover has been described above. The Basic Policy Wording is set out in form EIL (CAN) 1279 which is available through Brokers. The actual policy wording for a specific risk can, within certain defined limits, be written to provide for

specific requirements associated with individual risks.

The policy is, as previously noted, written on a "claims made" basis and is for a twelve month policy period. Renewal is subject to a technical "renewal" report which is prepared and paid for by the insurers.

Bearing in mind the fact that many environmental incidents involving waste disposal sites have in fact occurred subsequent to the active life of the site in question, the subject of a "discovery period" was of major concern in the study. Here again the response of the insurers has been generally positive. They have indicated a willingness to provide for a discovery period of up to five years, although this will probably require consideration on a case by case basis particularly as regards the additional premium that will undoubtedly be involved.

In the ownership, operation and use of a waste disposal facility, a number of different parties are often involved, each of whom may have an insurable interest in the facility or operation. A policy can be written to cover such an eventuality, each such party being a named insured. Also the policy can, subject to the approval of the insurers, be transferable to a new owner or operator, or be extended to cover the interests of additional parties.

It is not uncommon for Group Insurance Programs to be developed to cover associations or groups of individuals or organizations having similar occupations or interests. It is understood that the insurers would be willing to consider such an approach should Legislation or an increasing awareness of the liability exposures involved result in a more general demand for this type of insurance. It is perhaps worthy of note that a Group Insurance Plan for truckers has in fact been established by a Truckers Association in the United States. Also a Group Insurance Program is in place in Canada to provide this type of Insurance to municipalities.

Following a review of the premium Indications received for two specific operations, it was requested by officials of the Ministry of the Environment that information be assembled to provide some preliminary

indications of the possible financial impact if all municipal disposal sites in the Province were required by law to carry the insurance described.

With the assistance of the insurers a rating system was developed based on size of municipality on a population basis. These rates are the maximum per capita insurance rates that would normally be applied to sanitary landfill operations involving domestic and commercial solid wastes only. The disposal of liquid, hazardous, hospital and other similar types of waste was specifically excluded. These rates were then applied to the population statistics in the 1977-78 Municipal Directory published by the Ontario Ministry of Treasury, Economics and Intergovernmental Affairs. The limits of liability used were \$1,000,000 for any one claim with an aggregate of \$2,000,000 in any one year or policy period. Deductibles varied from \$2,500 for the smaller municipal units to a maximum of \$25,000. No allowance was made for a discovery period, and incidents involving sudden and accidental occurrences were assumed to be covered under appropriate comprehensive general liability insurance.

The Municipal Directory provides statistical classifications of the municipalities by Upper Tier (metropolitan, regional, district, counties, regions) and the Lower Tier (cities, boroughs, separated towns, towns, villages, townships, improvement districts). The per capita premium rates referred to above were applied to both these sets of statistics and the total premiums calculated were in round figures as follows:-

Based on Upper Tier Municipal Classifications	\$697,000
Based on Lower Tier Municipal Classifications	\$1,801,000

The wide spread in these two figures reflects the higher per capita insurance rates applicable to smaller municipal units which predominate in the Lower Tier Classification. In actual practice insurance cover would most likely be carried by municipalities in the Upper Tier Classification, to whom responsibility for solid waste disposal has in many cases been assigned. It would therefore be reasonable to assume that, based on the factors enumerated above that have been used in these calculations, the actual total costs would be in the order of

\$1.25 million. A further reduction in this amount could be achieved if the environmental risks associated with some of the major disposal operations prove such as to permit the use of lower per capita premium rates.

Limits in excess of the \$1M/2M used for the above calculations are available through the Environmental Impairment Liability Insurance program up to \$10M/20M. Limits in excess of these figures are subject to special negotiations.

The deductibles referred to are the minimum normally available to the various sizes of municipality. The use of higher deductibles will normally result in lower premiums.

As noted, these premiums do not provide for a five year period of discovery as the premium loading to cover this requirement will vary depending on site specific conditions.

The above provides a brief summary of the study undertaken for the Ministry of the Environment. For a more detailed explanation of the insurance program described, reference should be made to available literature which describes in detail its history, development, and the insuring agreement.

INVESTIGATIONS OF SUBSURFACE CONTAMINANT MIGRATION IN SAND AQUIFERS AT LANDFILL SITES

John A. Cherry
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario
N2L 3G1

ABSTRACT

During the past five years the Hydrogeological Research Group at the University of Waterloo has been investigating the processes of subsurface contaminant migration at several landfills. This paper provides a summary of the results obtained at three landfill sites located on permeable sand aquifers in Ontario. The oldest of these landfills began operation in 1940 and was abandoned in 1976. The other two sites began operation in 1960 and 1970 and are still active. At each site a zone of contaminated groundwater has moved a distance of 700 to 800 m from the landfill. At two of the sites, the contaminated water has remained entirely below ground surface. At the third site, contaminated groundwater feeds springs that drain into a local stream. The plumes of contaminated groundwater are characterized by concentrations of chloride, bicarbonate, sodium, calcium, magnesium, iron, and dissolved organic carbon at levels well above background concentrations. Processes of attenuation in the aquifers cause each of these constituents to decline considerably in concentration in the directions of groundwater flow. Toxic heavy metals and non-metals such as arsenic and selenium have not been observed in the plumes at two of the sites; insufficient data on these constituents is available from the third site. There is no indication at present that the plumes have caused significant degradation of water resources used by man; however, little is known about the composition or effects of organic compounds that comprise the dissolved inorganic carbon.

INTRODUCTION

In recent years in Ontario and in many other parts of North America, the selection of sites for sanitary landfills has become a controversial issue. Much of the controversy that is associated with many new sites pertains to actual or perceived hazards related to the possibilities of off-site movement of landfill-derived contaminants in groundwater. This concern is most relevant in the humid or sub-humid climatic regions of North America because in these regions water from rain and snow infiltrates through the landfill refuse and commonly causes leachate to seep from the landfill into the underlying groundwater regime.

Nearly all sanitary landfills in Ontario are situated on Quaternary deposits that were deposited during the Pleistocene Epoch by glaciers or by rivers or lakes formed by glacial meltwater. These deposits can be grouped in four main categories: gravel, sand, silt and clay. When landfills are situated on deposits that are composed of clay and silt (such as clayey or silty glacial till or glacial lacustrine clay), there is generally little possibility of extensive migration of contaminants in groundwater. This is the case because groundwater flow in these deposits is generally very slow. When landfills are located on deposits of sand or gravel, however, groundwater flow rates are commonly high (from tens of centimetres per day or to many metres per day) and landfill-derived contaminants may move large distances beyond the site boundaries in the groundwater zone. Because rain and snowmelt infiltrate through landfills even after the landfills are covered over with earth and are seeded to grass or trees, leachate continues to be produced after they are abandoned. Zones of groundwater contamination can undergo expansion for many decades or even hundreds of years.

The purpose of this paper is to provide a brief overview of some of the results of investigations of contaminant occurrence and migration of contaminants in groundwater at sanitary landfills situated on deposits of permeable sand in Ontario. These investiga-

tions, which are being conducted by the University of Waterloo with funding now provided mainly by the Ontario Ministry of the Environment began in 1976 at an abandoned landfill at the Canadian Forces Base at Borden, Ontario, and in 1980 were extended to include the landfill that serves the city of North Bay and the Woolwich landfill near Elmira in the Regional Municipality of Waterloo. The objective of these investigations is threefold: 1) to develop improved methods for monitoring contaminant migration in groundwater at landfills, 2) to develop a better understanding of the physical and chemical processes that cause attenuation of landfill-derived contaminants in groundwater and 3) to appraise and develop models for prediction of contaminant migration in permeable sandy deposits.

DESCRIPTION OF THE STUDY SITES

The development of extensive zones of contaminated groundwater at landfills normally takes many years or decades and thus little can be learned by monitoring a new landfill for only a year or two just after landfilling begins. An alternative approach that we are pursuing is the monitoring of groundwater zones that have been receiving landfill leachate for many years or decades so that the long-term effects on groundwater can be determined by only a few years of monitoring.

To date, the investigation has included three landfills, referred to as the Borden, North Bay and Woolwich landfills. The landfills differ considerably in age and size but they are not much different in refuse thickness. At each site the refuse is situated in unconsolidated sand. At the Borden and North Bay sites the bottom of the refuse is near or just slightly below the water table. At the Woolwich site the bottom of the refuse is 5 to 10 m above the water table. At each site sand excavated from the site or from nearby areas was used to cover the refuse. Landfilling at the Borden site began in 1940 and ceased in 1976, at which time the landfill received a final sand cover that was seeded with grass. The North Bay and Woolwich landfills began operation in

1960 and 1970, respectively, and they are continuing to receive refuse. Nearly all of the landfilled areas at these sites are at their final levels and have received sand cover. Part of the landfilled area at the North Bay site has also received sewage sludge and sawmill cuttings. The permeable sand cover on each of the landfills and the flat or only gently sloping surface over much of the landfilled areas are features conducive to infiltration of water from rain and snowmelt through the refuse. This causes leachate to move downward to the water table.

The Borden landfill received normal household and cafeteria wastes and building construction debris from the Canadian Forces Base Borden which, until 1976, the landfill served as the only operational dump site during the post World War II period.

METHODS OF INVESTIGATION

Field studies at the Borden site included geological test drilling, stratigraphic coring, geophysical surveys, installation of conventional piezometers and standpipes, installation of multilevel point samplers and bundle-type multilevel piezometers, periodic water-level and water-quality monitoring, and groundwater-temperature surveys. These investigations are described in detail by Waterloo Research Institute (1980). Similar investigative techniques were used at the Woolwich and North Bay sites, with the exception of stratigraphic coring and geophysical and temperature surveys. To date, the Woolwich and North Bay sites have been monitored in less spatial detail and less frequently than the Borden site; however, the investigations at these two sites will continue for one or two more years, whereas the investigation of the Borden landfill is nearly complete.

In the initial phase of groundwater monitoring at two of the sites (Borden, 1974-75; Woolwich, 1975) conventional standpipe piezometers and water-table standpipes installed using hollow-stem augers were used. Based on this experience it was concluded that more cost-effective monitoring devices were needed to achieve detailed three-

dimensional monitoring of the water chemistry in the sand aquifers at each site. Several groundwater monitoring devices were then developed or adapted for the investigation, two of which are shown in Fig. 1. The multilevel point sampler is described in detail by Pickens et al. (1978). The bundle-type piezometer is described by the Waterloo Research Institute (1980).

The multilevel samplers shown in Fig. 1 enable water samples to be acquired from different levels at a single borehole in a sand aquifer. Each of these monitoring devices consists of a cluster of polyethylene or polypropylene tubes attached to a PVC pipe, either inside or outside the pipe. Each tube in the cluster extends to a different depth below the water table so that when the cluster of tubes is sampled by vacuum pumping, a vertical profile of chemical composition can be obtained at the monitoring site. At sites where the water table is deeper than the limit for suction sampling, the bundle piezometers are sampled using a narrower tube and check valve as a bailer.

At each of the landfills, networks of multilevel point samplers and/or bundle piezometers were installed in stages. During each stage a number of the devices were installed and then sampled so that information on location of the zones of contamination was obtained. Upon evaluation of the concentration patterns, appropriate locations were selected for installation of monitoring devices in the next stage of drilling. By staging the installation program for monitoring devices in this manner, the monitoring networks that were developed after several stages provided more detailed information on the contaminated zones than would otherwise have been the case.

Each monitoring site with a multilevel point sampler or a bundle piezometer has between nine and 25 sampling points. With many of these devices at each landfill site, the total number of sampling points at each site is large. All of the sampling points were sampled and analysed for electrical conductance and chloride, both of which can be done quickly at low expense. At each of the sites, these two parameters provided an indication of the presence or absence of leachate contamination in the aquifer. After delineating the general patterns of contami-

nation in the sand aquifers, a representative group of sampling points at each site was sampled for analysis of a large number of dissolved inorganic constituents, including major ions, minor constituents, and trace elements. When these samples were collected, the water was filtered as soon as it was withdrawn from the aquifer. Samples for cation and trace element analyses were then immediately acidified to prevent chemical changes prior to laboratory analysis. The analyses of samples from the Borden and North Bay sites were conducted in the water quality laboratories of the Ontario Ministry of the Environment. Samples from the Woolwich site were analysed in the laboratories of The Regional Municipality of water.

PATTERNS OF GROUNDWATER CONTAMINATION

The occurrences of contaminated groundwater, identified by electrical conductance and chloride concentrations, in the sand aquifers at the three sites are shown in plan view and along cross sections in Figures 2-7. The data upon which the Borden diagrams are based are presented by MacFarlane (1980) and by the Waterloo Research Institute (1980). The data pertaining to the Woolwich and North Bay sites will be included in reports and theses that will be prepared in 1981 and 1982.

At each of the sites a plume of contaminated groundwater originates at the landfill and extends a distance of 700 to 800 m in the direction of the regional water table slope. Each of the contaminant plumes travels along the bottom of the aquifer. Deeper movement of the contaminated water is prevented by deposits of glacial till or glaciolacustrine clay that have a much lower hydraulic conductivity than the aquifers. The Borden plume is fan-shaped because during the spring and early summer, mounding of the water table beneath the landfill causes groundwater flowlines to extend in a radial pattern from the landfill. In contrast, the North Bay and Woolwich plumes are narrow because of the lack of extensive influence of water-table mounding beneath the

landfill and because of the uniformly sloping regional water table.

The position of the front of the plume at the Borden site (Fig. 2) is well-defined because numerous monitoring devices are located in the vicinity of the front and because the monitoring devices were sampled on various occasions during 1977-1980. The average northward velocity of groundwater in the aquifer in the vicinity of the plume front is approximately 50 to 75 metres per year. Comparison of concentration patterns for several years suggests, however, that the identifiable plume front is advancing at a much slower rate. This condition is attributed to mixing (dispersion), which causes the plume to dissipate as it advances.

At the North Bay site the leachate springs located near the stream about 800 m southwest landfill probably represent the front and exit zone of the plume. Although a definitive interpretation cannot be developed at present because there are insufficient monitoring devices in the vicinity of the springs, it appears that the plume will advance no further.

At the Woolwich site the plume has been traced southward for a distance of about 800 m from the landfill. The front of the plume however, has not yet been delineated. It is expected that this will be accomplished in the next stage of installation of monitoring devices. The existing data indicate that the plume has undergone considerable attenuation along the 800 m of travel distance. In comparison to the Borden and North Bay sites it is much more costly and time-consuming to accurately delineate the plume at the Woolwich site because the depth to the bottom of the aquifer is much greater, thereby causing greater drilling costs, and because the depth to the water table is also much greater, which causes water sampling to be much more tedious.

WATER QUALITY IN THE CONTAMINATED ZONES

In terms of percentage of the total dissolved solids in the contaminated zones at the three sites, the dominant inorganic

constituents are chloride, bicarbonate, sodium, calcium, magnesium, and iron. The Borden site differs from the other two sites in that sulfate is also a major component of the dissolved solids. Although these major inorganic species cause the water to differ considerably from the natural groundwater in the aquifers and although some of these species cause the water to be unsuitable for domestic use, they are not toxic to humans and they do not represent an appreciable hazard to the biosphere. If water quality is judged on these constituents alone, it would be reasonable to conclude that there are many other activities of man that cause groundwater to become as unpotable as at these landfills but over much larger areas than is affected by landfills.

Numerous groundwater samples from the Borden and North Bay sites were analysed for heavy metals and other hazardous inorganic constituents such as arsenic, selenium, and fluoride. We have found no evidence to indicate that the plumes contain any toxic metals or non-metals at concentrations that generally exceed the limits recommended by provincial or federal guidelines for drinking water. It is reasonable to conclude that these constituents are not being leached from the refuse at significant rates or that they are being removed from the leachate by geochemical processes in the sand immediately beneath the landfills. This may be occurring as a result of precipitation, co-precipitation, and adsorption. Insufficient data are available at the present time to determine whether toxic metals or non-metals at the Woolwich site occur in the contaminant plume beyond the site boundaries.

In addition to the analyses of numerous dissolved inorganic species in the contaminated groundwater, the samples were analysed for total dissolved inorganic carbon (DOC). Each of the plumes has DOC concentrations that are considerably above background concentrations in the aquifers. The elevated concentrations extend throughout the plumes with declining concentrations towards the frontal positions of the plumes. The dissolved organic carbon has probably been derived from food wastes, plastic manufactured materials, and possibly liquid

industrial wastes. Investigations have recently been initiated with a view to identifying many of the organic compounds that comprise selected fractions of the dissolved organic matter. Until the nature and toxicity of the dissolved organic matter in the contaminant plumes is known, it will not be possible to assess potential long-term environmental effects of landfilling at sites located on sand or gravel aquifers in areas where groundwater pumping occurs or where groundwater feeds surface water courses.

DISCUSSION

The results obtained from the investigations of the three landfill sites indicate that landfills on sand aquifers can produce zones of contaminated groundwater that extend many hundreds of metres beyond the site boundaries. As the fronts of the contaminant zones advance, mixing (i.e. dispersion) causes the concentrations of the dominant constituents in the plume to decline considerably. The results obtained from the Borden site suggest that in some cases mixing may cause the plume to dissipate to the extent that the rate of advance becomes very slow relative to the rate of groundwater flow.

At the Borden and North Bay sites, no water-supply wells exist in the aquifers through which the plumes are moving. At the Borden site, water-supply wells are located in deeper aquifers that are isolated from the shallow aquifer by extensive clay beds. At the North Bay sites local wells are in bedrock and the population pattern is such that the zone of groundwater contamination is of no consequence at present. At the Woolwich site, no water-supply wells have been affected by the plume. Studies are underway to determine whether any of the existing wells in the rural area may be affected at some time in the future.

At all three sites, zones of contaminated groundwater have migrated a considerable distance from the boundaries of the landfill areas. In terms of the criteria that are commonly used for assessing

landfill sites, the sites can be judged to be inappropriate for land-filling.

To avoid offsite movement of leachate in groundwater, many of the new landfills that have been developed in Ontario in recent years are situated on clayey deposits. Because of the climatic conditions that exist in Ontario and the nature of soil material often used for cover material, leachate normally forms in these landfills. Because the leachate cannot seep rapidly into the underlying clayey geological deposits as would occur at sandy sites, leachate mounding and side springs will develop unless the landfill design includes leachate collector drains, sumps, or pumps and provision for leachate passage to municipal sewage treatment plants or to other discharge points to rivers or lakes. If the leachate that is collected from the landfill is routed through a sewer system to a sewage treatment plant, many of the constituents in the leachate pass through the plant with little or no degradation. From the plant, they enter lakes or rivers. If this approach to landfill and leachate management is adopted, sewage treatment plant capacity is utilized and must continue to be utilized for many decades or hundreds of years in order to avoid direct discharge of leachate to the environment.

When appraising options for landfill siting in Ontario, it is appropriate to recognize that offsite movement of leachate is generally unavoidable and that the movement can occur by way of leachate drains, collector systems, ditches, and then by way of sewers to sewage plants or directly to surface waters. Or the offsite movement can occur via the groundwater zone to surface water, or to water supply wells. Regardless of the approach taken, there will eventually be a flux of landfill - derived contaminants to the biosphere.

In this context it is interesting to re-consider the results of the investigations of the three landfills reported on in this paper. Landfilling at the Borden site commenced 40 years ago and yet since this time leachate has not had any influence on surface water and there is little possibility that it ever will significantly influence surface water. The plume has influenced groundwater quality

but because alternative aquifers are available for water supply, this influence has had no affect on the local population. It probably never will as long as the shallow aquifer is not chosen for any consumptive use.

The North Bay landfill has caused contaminants to move through the aquifer and, after considerable attenuation, enter the local surface water drainage system. The sand aquifer has, in a sense, performed the same function as a sewage treatment plant, except that it has probably 'treated' the water to a greater degree. Unfortunately in esthetic terms offsite movement of leachate in the aquifer has caused degradation of some parts of the surface environment in a land area that is at present not owned by the owner of the landfill. If the land area to the south and southwest of the landfill had been originally included as part of the landfill site, the overall consequences of the subsurface migration of contaminants to the local springs and seeps could conceivably have been regarded as a favorable form of water treatment. An uncertainty that currently exists in this regard relates to the dissolved organic compounds in the seepage. Until the organic matter is adequately characterized, there will continue to be some uncertainty with respect to the potential for the contaminated seepage from springs to have an adverse influence on the local stream.

At present less is known about the water quality in the plume at the Woolwich site and of the potential for the plume to eventually advance into areas where water-supply wells currently exist. If the plume follows a pathway that does not intersect existing wells, then it will probably have no significant environmental consequence, even after many decades or longer.

SUMMARY AND CONCLUSIONS

At each of the three landfill sites reported on in this paper, a plume of contaminated groundwater has moved in the sand aquifer many hundreds of metres from the site boundaries. The dominant dissolved

constituents in the plumes are chloride, bicarbonate, sodium, calcium, magnesium and iron. Heavy metals and non-metals have not been identified at hazardous concentration levels in the plumes at the Borden and Woolwich site. Insufficient data is available on these constituents at the Woolwich site. At each of the sites, dissolved organic carbon at concentrations above background occurs throughout the plumes. Investigations aimed at identifying many of the organic compounds that comprise this organic matter have recently been initiated.

ACKNOWLEDGEMENTS

Numerous faculty members, technicians and graduate students have participated in the investigations of the landfill sites described in this paper. Those that were involved in the Borden investigation are authors and co-authors of papers in the Waterloo Research Institute (1980) volume listed below. The results of the Woolwich and North Bay studies are as yet unpublished. The investigations of these two sites have been undertaken primarily by Paul Buszka, Janet Hewetson, Paul Johnson and Scott King.

Financial support for these studies has been provided by The Ontario Ministry of the Environment and by Environment Canada.

REFERENCES CITED

Pickens, J.F., J.A. Cherry, G.E. Grisak, W.F. Merritt, and B.A. Risto, 1978. A multilevel device for ground-water sampling and piezometric monitoring, *Ground Water*, Vol. 16, No. 5, p. 322-327.

Waterloo Research Institute, 1980. CFB Borden Landfill Study, Vol. 1, Hydrogeological Studies of A Sandy Aquifer A. An abandoned Landfill (this volume comprises eight chapters by different authors).

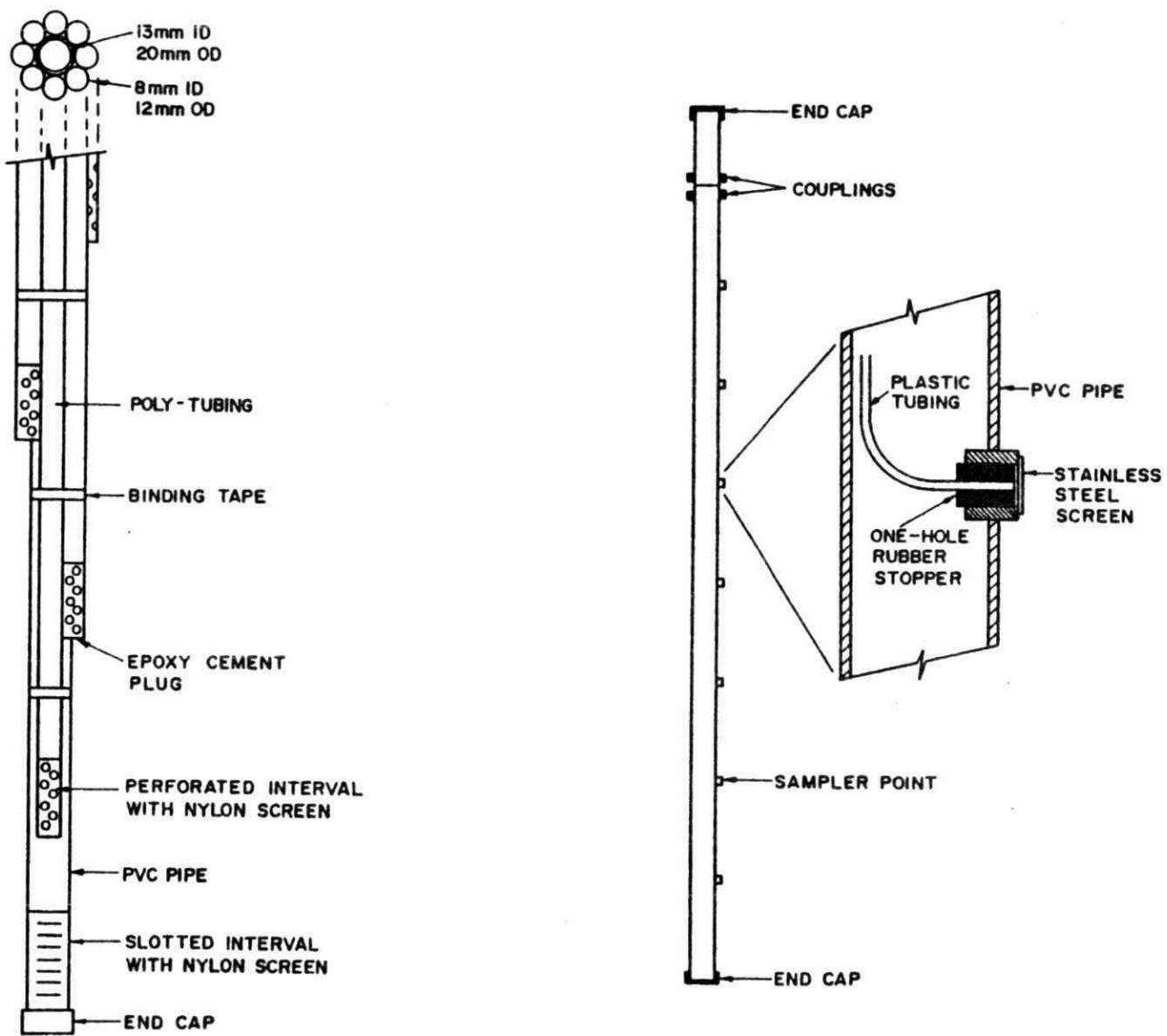


Figure 1. Schematic diagrams of a bundle piezometers and a multilevel point sampler.

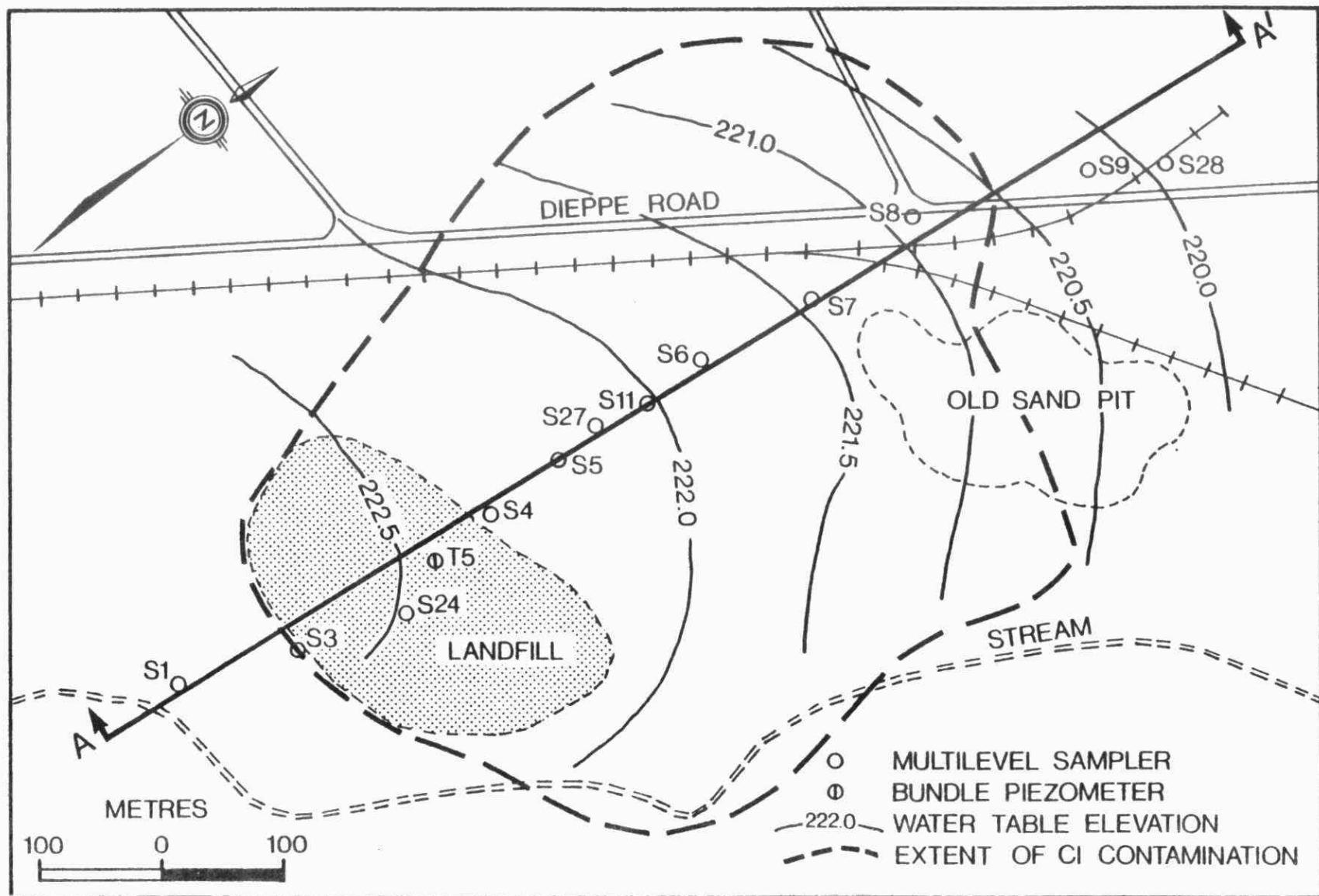


Figure 2. Area of contaminated groundwater, water-table contours, and sampling sites used in detailed hydrogeochemical studies at the Borden Landfill.

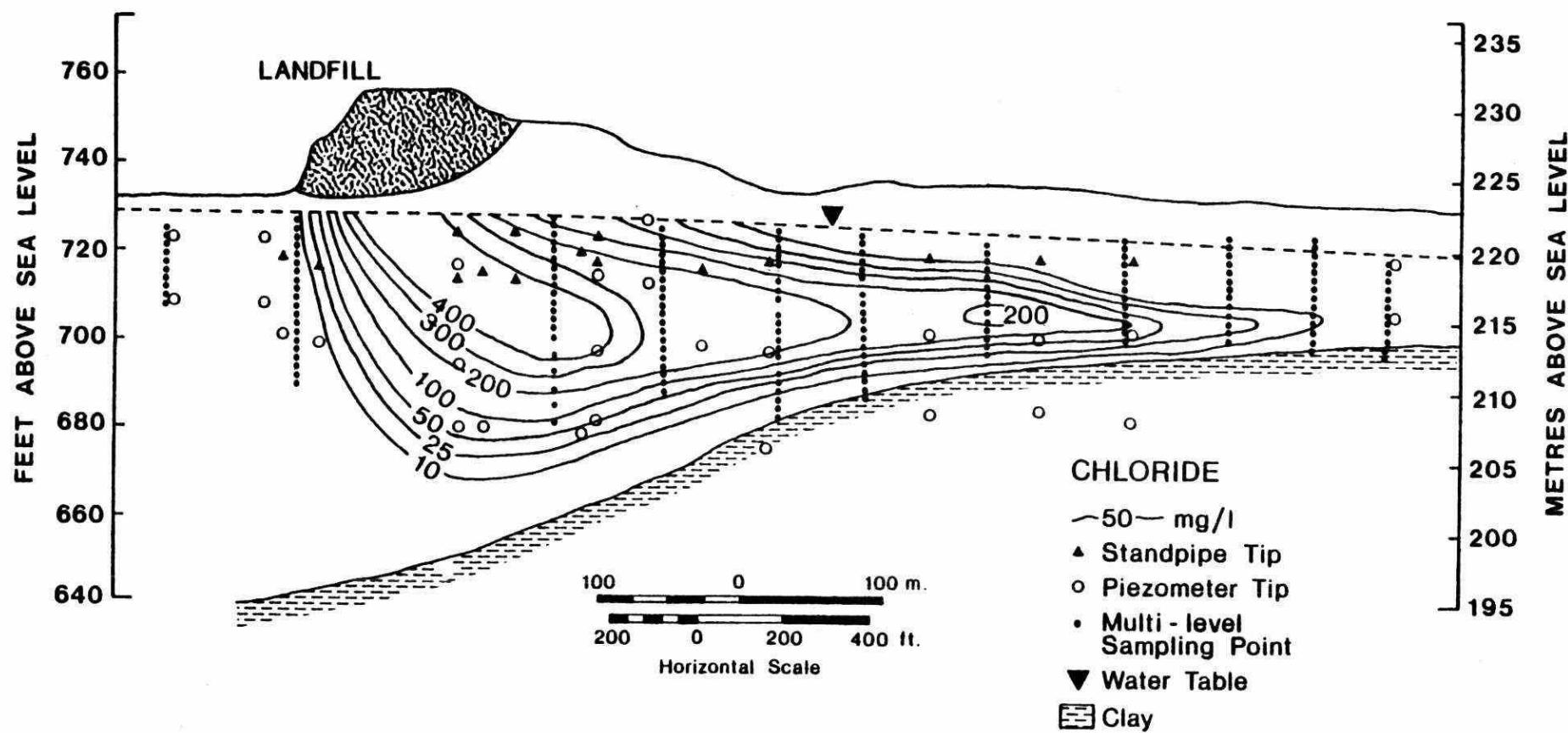


Figure 3. Distribution of chloride along a longitudinal cross section through the Borden site.

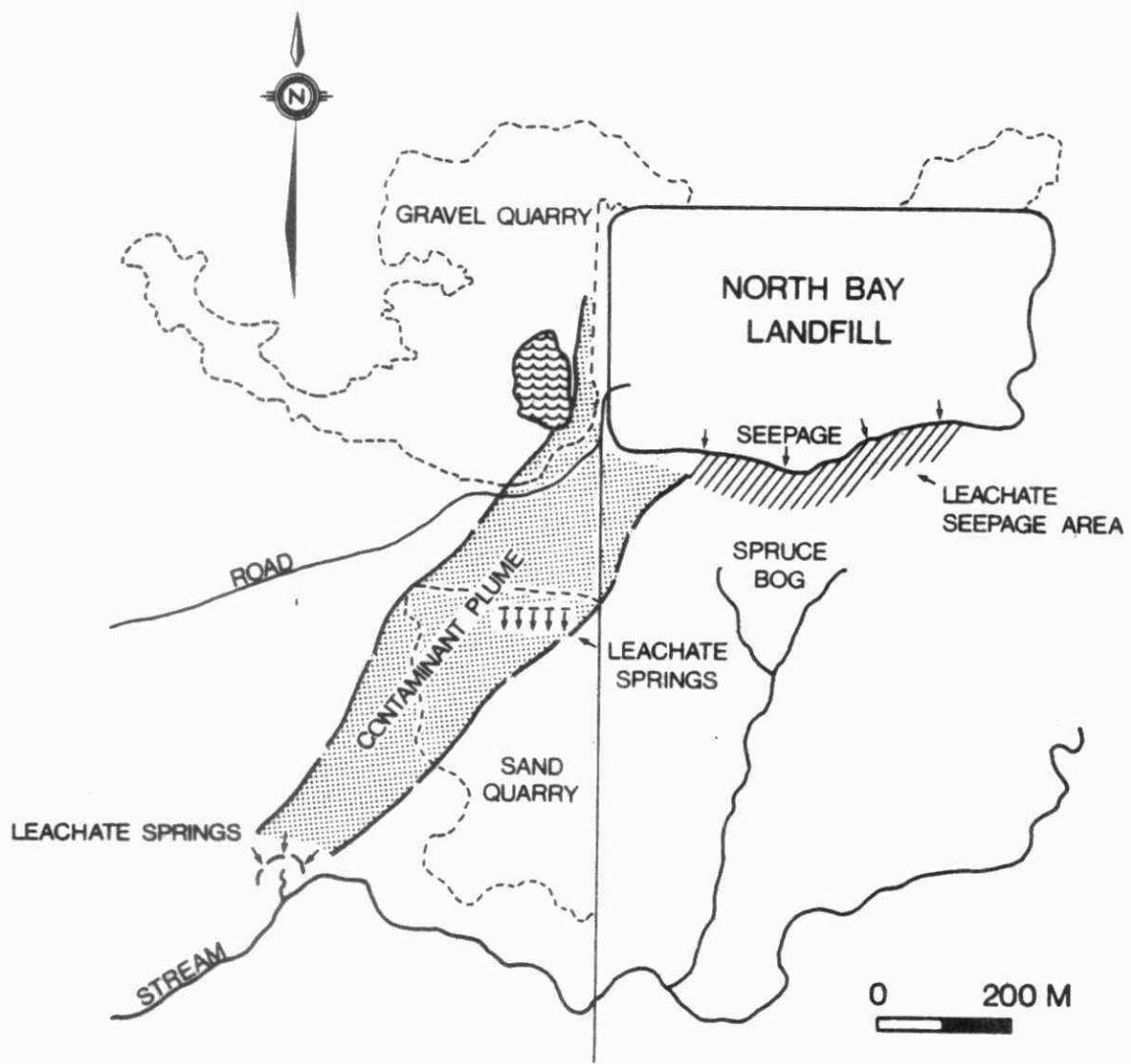


Figure 4. Area of contaminated groundwater and other hydrologic features at the North Bay Landfill.

GROUNDWATER CONTAMINATION NORTH BAY LANDFILL

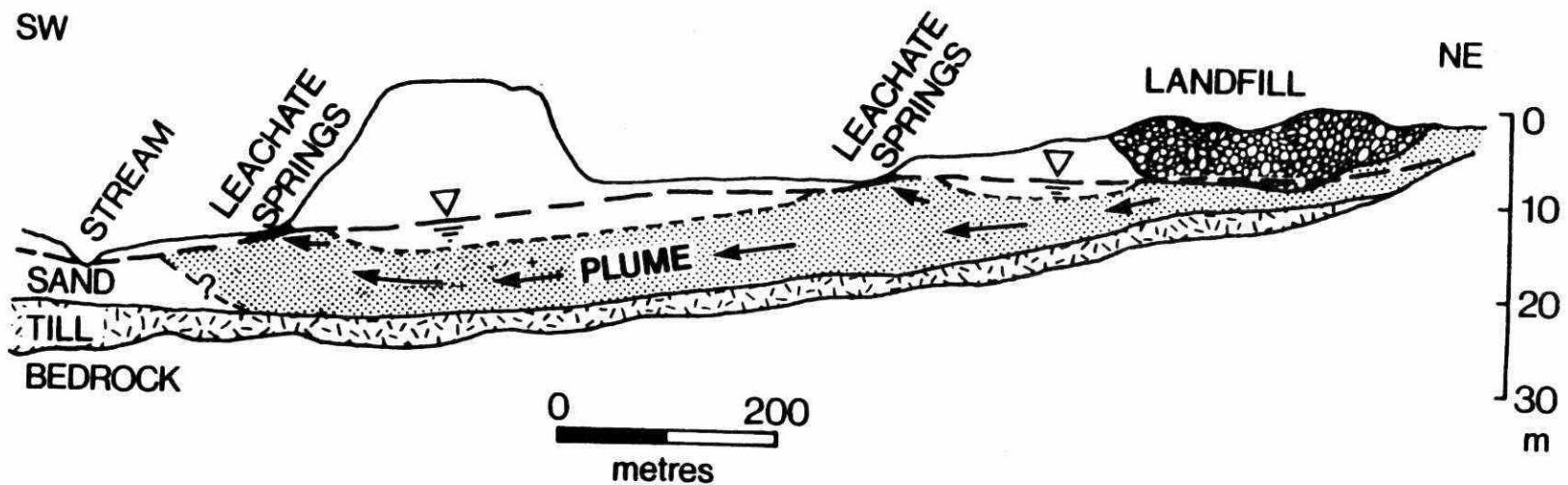


Figure 5. Zone of contaminated groundwater and leachate springs displayed on a longitudinal cross section through the North Bay landfill site.

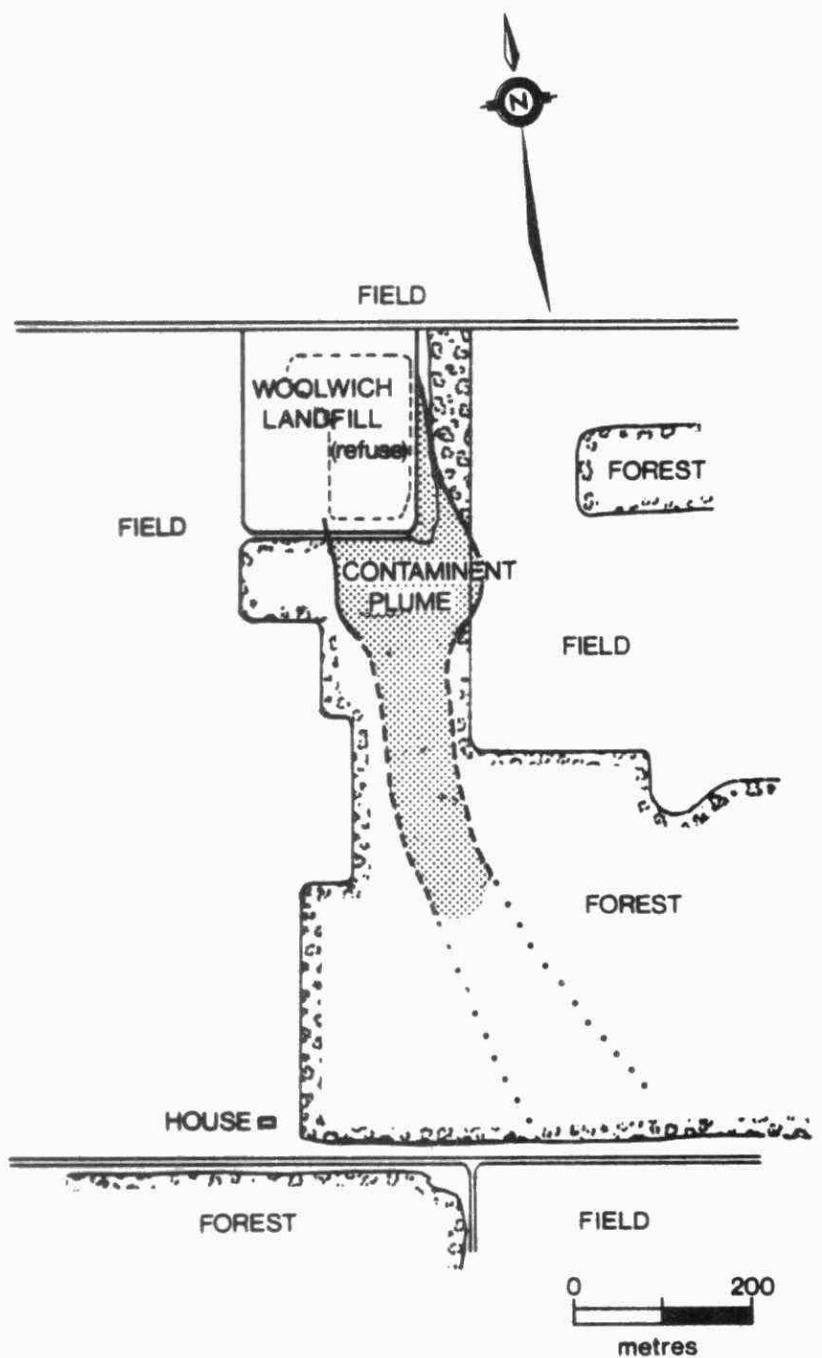


Figure 6. Area of contaminated groundwater at the Woolwich landfill in the Regional Municipality of Waterloo.

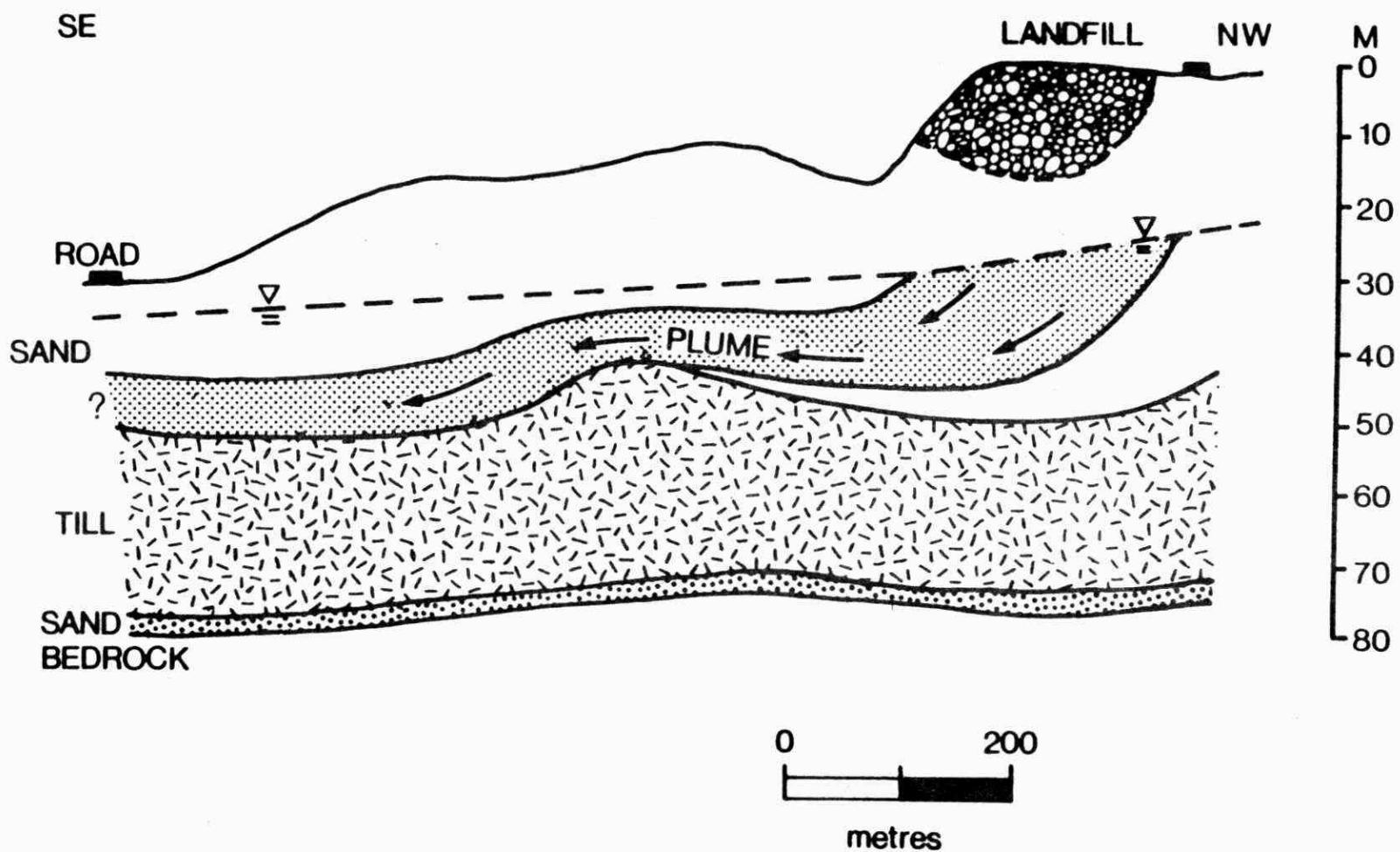


Figure 7. Zone of contaminated groundwater displayed as a longitudinal cross section through the Woolwich landfill.

ORGANIC CONTAMINANT REMOVAL IN DRINKING
WATER - AN OVERVIEW

By:

K.J. Roberts
Water Technology Section
Pollution Control Branch
Ontario Ministry of the Environment

Nov. 25/80

ORGANIC CONTAMINANT REMOVAL IN DRINKING
WATER - AN OVERVIEW

BY:

K.J. Roberts

1. INTRODUCTION

Preamble

The results of surveys of trace organics in drinking water (1-3), epidemiological surveys associating such organics with increased cancer risk (4), and the recently published guidelines for Canadian Drinking Water Quality, 1978, (5) which contains a guideline for trihalomethanes, and the regulations promulgated by the United States Environmental Protection Agency (6) have all contributed to an increased interest in methods for evaluating a water supply and its exposure to organic contaminants. The risk associated with the presence of organic contaminants in a drinking water (7) and the determination of appropriate methods for treatment have consequently received considerable attention (8,9).

General

The organic compounds that have been identified in drinking water make up a small fraction of the total organic matter present. About 90% of the volatile organic compounds have been identified and quantified but these represent no more than 10% by weight of the total organic material. Only 5-10% of the non-volatile organic compounds, that comprise the remaining 90% of the total organic material, have been identified.

More than 700 specific organic chemicals have been identified in various drinking water supplies. These compounds result from such diverse sources as industrial and municipal discharges, urban and rural runoff, and natural decomposition of vegetative and animal matter, as well as from water and sewage chlorination practices. Compositions and concentrations vary from virtually nil in protected groundwater to substantial levels in many surface waters and contaminated groundwaters.

Organic chemical contaminants in drinking water can be divided into two major classes: those of natural origin and those of synthetic origin. The natural substances represent by far the greatest portion and consist primarily of undefined humus and fulvic materials and others produced by normal organic decomposition or biotic transformation and are not known to be harmful in themselves. Therefore it will be useful to focus attention on those organic chemicals of synthetic origin.

The synthetic chemicals in water can be sub-divided into two groups, the first group consists of those chemicals that result from water treatment practices (eg. trihalomethanes) (10). Recent studies indicate that except for certain cases trihalomethanes constitute the largest portion of the identifiable synthetic chemicals in drinking water. Unlike other synthetic chemicals, chloroform and other trihalomethanes are formed during the treatment process. They are thus found in virtually every drinking water supply that is disinfected by chlorine, and not uncommonly at concentrations in the hundreds of parts per billion. Studies have indicated that the trihalomethanes may represent only a portion of the total halogenated products of chlorination of water (11). Methods are being developed to quantify the total halogenated organic compounds produced during chlorination; however for other than the chlorinated phenols and a few other substances, identification is very difficult.

Halogenated organics such as carbon tetrachloride, chloroform and hexachloroethane have also been detected as parts per million levels as contaminants in chlorine. The method of manufacture of the chlorine determines the levels of contamination. It is obvious then the chlorine used for potable water disinfection must be of the highest purity to avoid introduction of contaminants into drinking water.

The second group of synthetic chemicals consists of those chemicals introduced as a result of point and non-point sources of pollution. Throughout North America both surface waters and to a lesser degree groundwaters are contaminated with a variety of these pollution related synthetic organic chemicals ranging from the lower molecular weight halogenated hydrocarbons and monocyclic aromatic compounds to higher molecular weight pesticides, polycyclic aromatic compounds.

The above classes of compounds have been found in drinking water using gas chromatography or gas chromatography/mass spectroscopy. However, many of the natural products and also high molecular weight synthetics in water are not amenable to detection by these commonly used methods. As mentioned before the organic contaminants which have been identified in drinking water constitute only a small percentage of the total amount of organic matter present.

Risk Assessment (12)

The hazards of ingesting chemical pollutants in drinking water can be assessed in two general ways: with epidemiological studies and with laboratory studies of toxicity. The aim of both types is to provide information on the risk to man. For such an assessment the average amount of water consumed per person is generally assumed to be two litres/day. The daily consumption of water however is a function of such factors as temperature, humidity and physical activity; these factors may vary widely.

Concerning the toxicity to man, there are certain principles which should be borne in mind when efforts to assess the effects of long continued exposure to chemical trace contaminants at low dose rates are made. Firstly, it is assumed that effects in animals, properly qualified, are applicable to man. Secondly, we do not now have methods existing to establish a threshold for the long term effects of toxic agents. Thirdly, that the exposure of experimental animals to toxic agents in high doses is a necessary and valid method of discovering possible carcinogenic hazards in man. And fourthly, that exposure to such chemical compounds should be assessed in terms of human risk, rather than as safe or unsafe. Risk only constitutes half of the essential comparison that should be made in the assessment of human hazard; the other half is the benefit to the exposed population of the agent for which hazard has been identified. It is not possible to guarantee a risk free society; nor is a risk free society necessarily the best society. It is often necessary to accept the

risks of chemicals such as drugs and pesticides when the benefits warrant their use. Risks imposed on persons who gain no benefits are generally not acceptable. Personal choice, personal values obviously must enter into any risk benefit comparison.

It should be noted that mankind is already exposed to many carcinogens whose presence in the environment cannot be easily controlled. In view of the nature of carcinogenic activity, the long latent period of its development, and the irreversibility of chemical carcinogenesis, it would be wrong to expose the general population to an increased risk if the benefits were small, questionable, or restricted to limited segments of the population.

The estimation of risk, is based upon many factors included in which are exposure, the dose, the animal data, chemical similarity and synergistic effects. These many parameters underline the fact that when taking into account the safety factor and the uncertainty factors involved because of lack of full data, the complexity of assessing the health implications of chemicals, even when the best available means are used, can result in widely varying risk assessments.

Through source and supply surveys, followed by source and supply analyses by GC/MS combination we can arrive at a measure of supply evaluation and from there, make a risk assessment.

If the risk assessment following the supply evaluation shows that some chemical substances are present which should preferably be removed from the water supply then a feasibility study should be conducted to determine the most cost effective means of providing a high quality water supply. There are a number of alternatives which might be considered to provide an adequate water supply. Firstly, we might attempt to find a protected source. Secondly, the elimination of contaminants from the present source should be pursued. Thirdly, a possible combination of off-line storage with river supplies so that water can be drawn off during periods of good quality. And fourthly, treat the water supply to remove the materials of concern. As with most problems facing the water industry we must deal with existing water plants and their treatment configurations and thus the

third mentioned alternative is not feasible in most situations in Ontario. Therefore it is with the fourth alternative, the treatment of chemicals of concern, that we have to deal with in most situations.

2. SYNTHETIC ORGANIC CHEMICALS

As outlined previously, the largest portion of synthetic organic chemicals found in drinking water are those formed by the reaction of organic precursors with the disinfectant used at the water treatment plant. In Ontario this disinfectant has traditionally been chlorine. Since the discovery (through improved analytical techniques) by Rook (10) of trihalomethanes in treated water considerable concern regarding their health effects and much experimental attention has been directed toward these organic chemicals.

Trihalomethanes

Trihalomethanes are members of a group of organic chemicals that contain one carbon atom, one hydrogen atom, and three halogen atoms. The halogen atoms important in the formation of trihalomethanes in water are chlorine, bromine and iodine; other halogens are not significant.

In most locations, only 4 of the ten possible trihalomethanes can occur in significant concentrations in chlorinated drinking water. However where iodide is naturally present in the water, several iodine containing trihalomethanes may also occur. The four trihalomethanes commonly associated with chlorination are as follows (13):

Trichloromethane (Chloroform)
Bromodichloromethane
Dibromochloromethane
Tribromomethane (Bromoform)

Trihalomethanes are formed by the reaction of free chlorine with certain organic compounds in the water. Formation occurs during chlorination and can continue to occur as long as free chlorine is available. The reacting organic compounds are called 'trihalomethane

precursors' or just 'precursors'. Trihalomethanes are frequently called chlorination by-products. The reaction is depicted as:



Precursors are organic compounds, primarily humic and fulvic acids produced from decaying vegetation; these are frequently called natural organics. Synthetic man-made organics are usually not trihalomethane precursors.

High concentrations of precursors can cause objectionable colour in water, can cause taste and odour problems and they can act as nutrients for microbiological growth. Precursors are significant because of their role in the formation of trihalomethanes and other disinfection by-products.

Since the natural organic precursors are more commonly found in surface water, water taken from a surface source is more likely than ground water to produce significant trihalomethane levels.

It will be useful to examine treatment methods to reduce trihalomethanes in finished water since many of the processes proposed will apply to other synthetic organic compounds also.

CONTROL OF TRIHALOMETHANES

There are three basic ways of controlling trihalomethanes in drinking water:

- 1) Treatment to reduce the precursor concentration prior to chlorination,
- 2) Use of a disinfectant that does not generate trihalomethanes in water,
- 3) Treatment to reduce the trihalomethane concentration after formation.

These control possibilities will be followed with further details being presented of the options available within each of the general categories.

Some definitions of the terms used when discussing THM's are necessary. These are:

- instantaneous trihalomethane concentrations; this is the concentration of trihalomethanes in the water at the moment of sampling.
- terminal trihalomethane concentration; this is the concentration of trihalomethanes that occur when a sample of water is stored for a specified time at a specified pH and temperature.
- trihalomethane formation potential; this is the difference between the terminal and the instantaneous trihalomethane concentrations.

Because there is no direct measurement for trihalomethane precursors, the degree of precursor removal must be judged by comparing trihalomethane concentration upon chlorination of an untreated control to similar data collected on a treated water after similar chlorination.

TRIHALOMETHANE PRECURSOR REMOVAL

The first control mode mentioned above, treatment to reduce precursor concentration prior to chlorination, is probably the one that has received the most attention. This is primarily due to the fact that modification of existing water plant unit operations is one of the most feasible alternatives. There are several options:

- a) Move the point of application of chlorine to as late in the treatment process as is practical so that most precursors are removed prior to chlorination,
- b) If chlorine is applied after coagulation and settling, or after settling and filtering, then improve these processes to optimize precursor removal. Such things as optimization of pH, polymer addition and mixing regimes would be advantageous in this consideration,
- c) Use an adsorbent, either powdered activated carbon, or granular activated carbon, for precursor removal prior to chlorination,

- d) Improve raw water quality or select an alternate source of water containing less precursor. Again as mentioned previously, this alternative is generally not a feasible one,
- e) Use a combination of the above, coupled with a reduction in chlorine dose if the reduction can be achieved without adversely affecting disinfection.

Moving the Point of Chlorination

Chlorine is applied at water treatment plants for a number of reasons. However, the primary reason for chlorine application during water treatment is for disinfection. The chlorine can be applied at various stages of the water treatment process. Often pre-chlorination is used in order to give more time for disinfection throughout the plant, and in order to keep bacterial growths and tastes and odours and so on, under control during treatment. Post-chlorination is used in order to adjust the chlorine residual prior to distribution and in order to achieve the final disinfection step. Moving the point of chlorination until after sedimentation for instance, would enable the removal of a significant portion of precursor material. This of course, places considerable emphasis on the post-chlorination step. The maintenance of microbiological quality during and following treatment modifications must be ensured. To this end, sanitary surveys of the system including biological evaluation of the source water are necessary. Additional monitoring to ensure the continued maintenance of optimal microbiological quality in finished water should be carried out until a steady state condition is reached. Also an active disinfectant residual should be demonstrated throughout the distribution system at all times during and after any treatment changes.

Coagulation, Sedimentation and Dual Media Filtration

We have already discussed the movement of the point of chlorination within the treatment scheme; the optimization of conventional pre-treatment processes can have a significant effect on the levels of trihalomethanes formed.

AbsorptionPowdered Activated Carbon (PAC)

PAC when used at practical dosage levels was not found to be particularly effective in removal of THM precursors. For example, at the impractical PAC dose of 100 mg/L one might expect up to 50% of the precursor material to remain after treatment.

Granular Activated Carbon (GAC)

GAC is very effective in removing organic material. The use of GAC for trihalomethane precursor removal has been studied (8,14). In many cases the water supplied to the GAC filter was coagulated and settled. Nevertheless exhaustion of the carbon was achieved in a relatively short time, ie. about 13 weeks for chloroform, 8 weeks for bromodichloromethane, 5 weeks for dibromochloromethane and probably less than two weeks for bromoform. The possible reason for the extremely short breakthrough time of bromoform might be that GAC does not remove bromide very effectively so that the bromide in the effluent plus the first breakthrough of precursor will form brominated trihalomethanes upon chlorination because the oxidation of bromide to bromine by chlorine followed by bromination occurs faster than the chlorination reaction. As the GAC ages and more precursor breakthrough chloroform will be produced.

Oxidation

Most work in this area has been carried out on three oxidants namely: ozone, chlorine dioxide and potassium permanganate.

Ozone when used at practical dosage levels has been found to be not particularly effective for removing trihalomethane precursors. Data compiled by Trussell et al (15) from independent work of several investigators showed that ozone precursor removal ranged from negative removal to up to 90% precursor removal. There are several variables which can account for the wide range of results: firstly of course the nature of the precursor, in addition the ozone dose, contact time, contact design and the dispersion system together with other water quality factors. The use of chlorine dioxide has shown some removal

of precursor material following the application of chlorine dioxide (16). The chlorine dioxide has some effect on the precursor such that it is changed so that it will not react with subsequent chlorine to form trihalomethanes. Precursor alteration/removals of up to 50% have been obtained when chlorine dioxide is applied in the disinfection dosage range of between 1 and 2 ppm. Experiments with potassium permanganate as a pre-oxidant have shown relatively small percent removals of precursor (17). Precursor removals as measured by potential trihalomethane formation have achieved maximum levels of only up to 20%. Again, it is thought that raw water quality and hence the kind of precursor material present will affect this process.

Table 1 (page 11) gives some indication of the effectiveness of various unit processes for reducing chloroform formation potential.

Aeration

In general aeration has not been found effective for reducing trihalomethane precursor materials from raw water at economical air to water ratios.

Biological Processes

The use of biological processes to break down organic chemicals has been given the renewed impetus in recent years. Riverbank filtration and slow sand filtration have been in use for many years and the quality of treated water has been high. Even at rates well above those usual for slow sand filtration, for example, up to 3 or 4 gal/min/ft² biological filtration has been successful in removing organics. More recently, in Europe, ozonation followed by activated carbon filtration has become a widely employed step in the water treatment process. This process commonly known as biological activated carbon or BAC has demonstrated that it can play an important role in the reduction of surrogates such as dissolved organic carbon and, to some extent, total organic chlorine.

TABLE 1

EFFECTIVENESS OF VARIOUS UNIT PROCESSES FOR REDUCING CHLOROFORM FORMATION POTENTIAL (11)

Process	Chloroform Formation Potential $\mu\text{g/L}$	Chloroform Formed $\mu\text{g/L}$	Remarks
Aeration followed by chlorination	66 ^a	66 ^a	Diffused-air aeration with air to water ratios up to 20:1 did not reduce chloroform formation potential (10 min. contact time)
Coagulation, Sedimentation and Dual-Media Filtration followed by Chlorination	48 ^b	13 ^b	
Coagulation, Sedimentation, Filtration/Adsorption by Granular Activated Carbon (5 min. contact time) followed by chlorination	48	≤ 1	GAC would be effective for 3 wks.
		≤ 10	GAC would be effective for 8 wks.
Powdered Activated Carbon added after Coagulation & Settling followed by chlorination	27 ^a	20 ^a	at PAC dosage - 8 mg/L
		9	at PAC dosage - 100 mg/L PAC contact time = 2-20 min.
Ozone only	48	None found	O_3 neither forms trihalomethanes, nor removes precursors at disinfection doses
Ozone followed by chlorination	48	48	Disinfection doses (≤ 1 mg/L)
Chlorine Dioxide only	74	≤ 1	ClO_2 does not form THM

Process	Chloroform Formation Potential mg/L	Chloroform Formed mg/L	Remarks
Coagulation, Sedimentation & Dual Media Filtration followed by:			
1) Chlorination	-	17 ^c	1.3 mg/L ClO ₂ and 1.5 mg/L Cl ₂
2) Chlorine dioxide with chlorine	-	3 ^d	THM formation decreases as the ratio of ClO ₂ to Cl ₂ increases

All tests performed on Ohio River water. Chloroform Formation Potential is the amount of chloroform formed when raw water is chlorinated past break-point and stored at 25° C for a specified contact time.

- a - chlorine contact time = 48 hours
- b - chlorine contact time = 96 hours
- c - chlorine contact time = 22 hours
- d - contact time for combination of chlorine dioxide with chlorine = 22 hours

ALTERNATE DISINFECTANTS

The benefits of, as well as the problems associated with, changing to some alternative method of disinfectant must be weighed. For example, ozonation, while not creating chloroform, also does not provide any residual disinfectant in the distribution system.

Since many of the alternative disinfectants or their corresponding by-products may have some undesirable properties, the first principle should be to apply whatever treatment is needed to provide water of high quality and low organic chemical content prior to the application of a disinfectant. In this way the chemical disinfectant demand of the water would be minimized and pathogen control will be maintained while disinfectant use and by-product formation will be minimized. At the present time a Provincial Lottery Funded programme is being carried out to study ozone as an alternate disinfectant, when used alone or in combination with chlorine, and to study in particular the by-products of ozone and examine their health related effects when in finished drinking water. Alternate disinfectants of course, include such oxidants as ozone, chlorine free chlorine dioxide, chloramines and to a lesser degree potassium permanganate. Ultraviolet disinfection has also been considered. It is important to reiterate that in all cases, residual disinfectant needs to be maintained throughout the distribution system.

Chlorine Dioxide

Chlorine dioxide may be a promising alternative to chlorine because a disinfectant residual can be maintained in a distribution system. This residual is reportedly comparable to chlorine as a biocide and, if the concentration of excess chlorine use to generate the chlorine dioxide can be kept low, the trihalomethane concentrations in the finished water will also be low.

There is some question concerning the health effects of ingesting chlorite iron. Chlorite converts hemoglobin to methemoglobin, and some health authorities have recommended the absence of chlorite in drinking water. Low dosages of chlorine dioxide of course have been used in the past for taste and odour problem eradication.

Ozone

Ozone is another effective disinfectant that does not produce trihalomethanes but it fails to provide a residual disinfectant in the distribution system and, like the other alternatives to chlorine, little is known about its organic by-products.

Chloramines (Chlorine plus Ammonia)

The use of a chlorine residual in a less active form such as chlorine combined with ammonia (chloramine or combined chlorine) will significantly reduce trihalomethane formation.

Combined chlorine is not as reactive as free chlorine for the formation of chloroform. Therefore if a utility adds ammonia in conjunction with chlorine addition or shortly thereafter, such that no free chlorine residual existed for long, while still being compatible with good disinfection, trihalomethane formation should be low.

Since chloramines are less active than free chlorine, chloramines are much less potent disinfectants than free chlorine. In fact, early studies, subsequently confirmed, demonstrated that chloramines required approximately a 100 fold increase in contact time to inactivate coliform bacteria and enteric pathogens as compared to free available chlorine (18). For this reason, chloramines are not recommended for use as primary disinfectants in drinking water treatment. Chloramine treatment finds its widest application in the maintenance of chlorine residuals in distribution systems, after the primary disinfection with free available chlorine or other disinfectants.

The microbiological quality of the finished product is still the foremost considered in drinking water treatment. Use of alternate disinfectants, therefore, must be an effective barrier against problem organisms while still bearing in mind the health effects of possible by-products.

TRIHALOMETHANE REMOVAL (after formation)

Trihalomethane removal can be achieved by granular activated carbon, however the bed life and consequent bed replacement is so low as to make the process non-viable in most cases.

Studies have been conducted on removing already formed trihalomethanes from drinking water by the use of PAC adsorption, ozonation, and treatment with chlorine dioxide. These processes were shown to be not particularly effective at removing trihalomethanes from the water.

With regard to the aeration treatment process it has been shown that particularly in the case of chloroform, which is volatile, the material will be lost from the water at any air/water interface.

Table 2 gives an indication of the effectiveness of various unit processes for the removal of chloroform from drinking water. As can be seen the aeration process appears the most viable of those indicated in terms of an on-going practical methodology.

TABLE 2
EFFECTIVENESS OF VARIOUS UNIT PROCESSES FOR
REDUCING CHLOROFORM IN DRINKING
WATER (11)

Process	Initial Chloroform Concentrations, μ g/L	50%	25%	10%
<u>Aeration</u>				
Air to Water Ratios for diffused-air aeration: 10 min. contact time	100	6:1	15:1	25:1
<u>Granular Activated Carbon</u>				
Expected life for 5 min. contact time	55	7 weeks	5 weeks	4 weeks
<u>Powdered Activated Carbon</u>				
Dosage, mg/L applied to: a) Chlorinated Raw Water b) Chlorinated, Coagulated and Settled Water	64 44	95 mg/L 27 mg/L	>105 mg/L 90 mg/L	>105 mg/L 105 mg/L
<u>Ozonation</u>				
4 min. contact time	Up to 25 mg/L O_3 had no effect on the chloroform concentration.			
<u>Chlorine Dioxide</u>				
Up to 48 hr. contact time	Up to 10 mg/L ClO_2 had no effect on the chloroform concentration.			

Synthetic Organic Chemicals - Industrial (Man-Made)

We have discussed the organics which might be present in water supplies, namely: naturally occurring organic substances such as humic and fulvic compounds; those organic chemicals, such as trihalomethanes, formed during water treatment and the final organics to be examined are those man-made synthetic organic chemicals present in a water supply. These include such compounds as pesticides and other organic constituents such as benzene, benzopyrene, carbon disulphide, carbon tetrachloride, pentachlorophenol, polychlorinated biphenyls, vinyl chloride which are industrially originated chemical compounds. Generally, many of the same unit processes as applied to trihalomethane and trihalomethane precursor removal apply in the case of the synthetic organic chemicals. A summary of the presently available treatment processes as outlined by Trussell and Trussell (9) is:

Aeration
diffused air
packed towers
Coagulation
Al 111
Fe 111
polymers
Oxidation
ozone
chlorine dioxide
permanganate
Biological Processes
riverbank treatment
biological active carbon
Adsorption
powdered activated carbon
granular activated carbon
synthetic organic carbon

It will be worthwhile to look at these treatment modes and their application to drinking water treatment in more detail.

Aeration

Aeration as a unit process for removal of organics has been inadequately evaluated to date. Work by McCarty et al (19) and by Singley et al (20) have demonstrated that air stripping can be effectively used to remove a variety of synthetic organic chemicals of a volatile nature. The efficiency and the material removed will

obviously depend upon the chemical quality of the water to be treated. It is important to note here that the significance of materials released to the atmosphere following air stripping needs further study.

Coagulation

Coagulation with metal salts has been used in drinking water treatment for many years. Coagulation is effective in removing many trace contaminants and is the main method for removal of colour in North America. It is an efficient means of removing aquatic organics of a humic origin during treatment thereby reducing the subsequent formation of trihalomethanes, however, little work has been done to evaluate the effectiveness of coagulation in the removal of the many synthetic organics of concern today. It is feasible that the coagulation process will be effective in removing high molecular weight organics especially those adsorbed on particulates but the removal of volatile organics would seem a more difficult proposition. As with many of the unit processes indicated the use of coagulation in combination with other processes might be needed to achieve specific results. Certainly coagulation can be optimized to achieve maximum organic carbon removal for each particular raw water quality.

Oxidation

The oxidation of synthetic organics through chlorination is clearly under considerable scrutiny today. The possibility of further chlorinated organics is a situation which is to be avoided. Examination of the effectiveness of the other three most common oxidants mentioned previously, that is, ozone, chlorine dioxide and potassium permanganate suggests that although each of these is somewhat effective with certain compounds, or with most compounds under the correct conditions, none of them seem applicable in the broad scope of drinking water treatment. In addition, again it must be borne in mind that by-products from these alternate disinfectants must receive detailed investigation before their general acceptability for use as a process alternative.

Biological Processes

The use of these processes has been outlined previously and is currently receiving close attention world-wide. This continued examination of such a treatment is necessary to ascertain the effectiveness in removal of the broad range of synthetic organics found in raw water supplies.

Adsorption

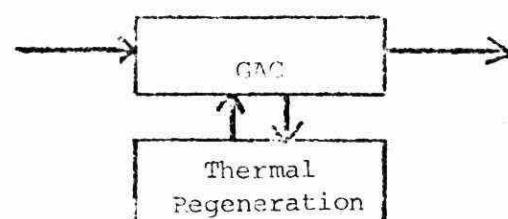
In terms of adsorption is has traditionally been the case in North America to employ PAC to remove trace organics especially those associated with taste and odour compounds. Recent evidence has shown that PAC is not a particularly broad spectrum process and is effective at removing only a small number of higher molecular weight compounds. In the same way synthetic organic resins have recently been evaluated; some of these have demonstrated effective removal of humic substances, some will remove low molecular weights synthetic organics, and others are particularly effective in trihalomethane removal. Many of these resins can be regenerated in-situ with steam, however, their high capital cost of selective removal characteristics make them border-line feasibility for use alone. Use in combination with other treatment unit operations can be effective.

Granular Activated Carbon (GAC) is presently the only unit process available that has a proven ability to remove a wide range of organic chemicals from aqueous solution. The mode of use of GAC will depend greatly on the type of organic chemical which is wished to be removed from solution. GAC can be used as replacement for the coal into the media filter or GAC contactors can be built as additional units to the conventional treatment processes.

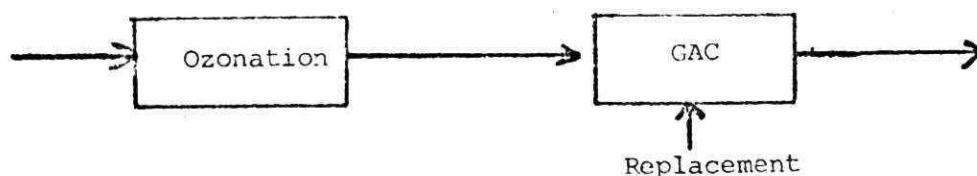
GAC can be used most effectively in the number of treatment combinations; these were outlined by Trussell and Trussell (9) in the following diagram.

Once again, effectiveness of each of these alternatives would depend greatly on the type of organic material to be removed from water and various other process variables.

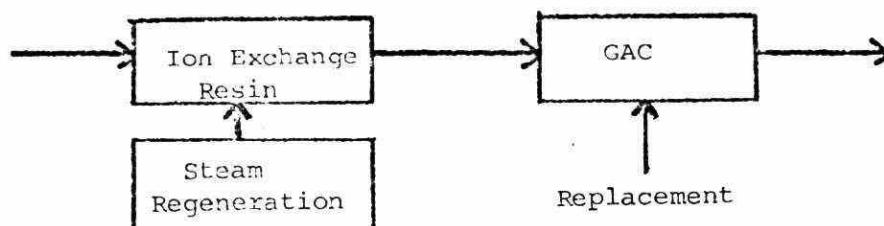
GAC Modes of Process Operation



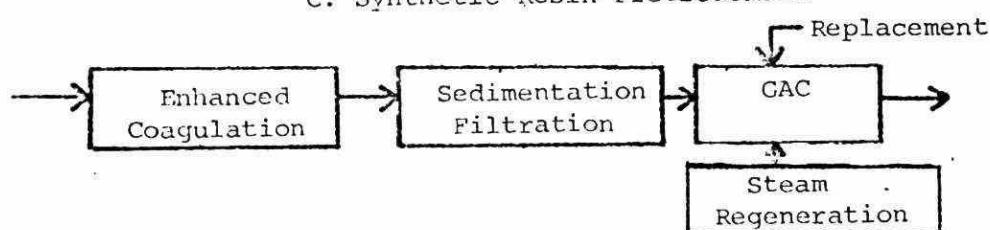
A. Conventional GAC



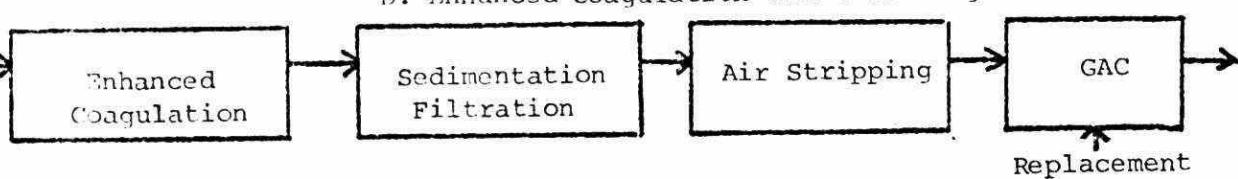
B. Ozone-Enhanced Biologically Active Carbon



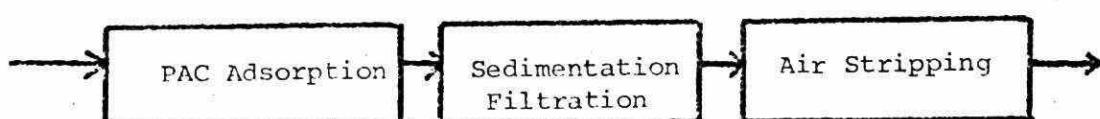
C. Synthetic Resin Pretreatment



D. Enhanced Coagulation and Steam Regeneration



E. Enhanced Coagulation, Air Stripping Conventional GAC



F. PAC adsorption, Air Stripping

All of these process alternatives should be evaluated using bench-scale, pilot-scale and field-scale pilot studies in order to better define their effectiveness and refine estimates of the capital and operational costs.

SUMMARY

This brief overview of organic contaminant removal in drinking water has looked at the two major classes of organic chemical contaminants in drinking water. These are: those of natural origin and those of synthetic origin. The synthetic chemicals were subdivided further into two groups. The first group, those chemicals that result from water treatment practices, and the second group, those synthetic organic chemicals resulting from our wide-spread use and manufacturer of synthetic organic chemicals. These chemicals have been, and are likely to continue to be, contaminants in our sources of drinking water and as such constitute some risk to the health of the consumer. We can obtain an estimate of the risk for many of the chemicals, whilst for many we have insufficient data to be able to estimate even at any very conservative extrapolation procedure, and thus we must continue to study these chemicals.

Treatment methods were outlined to deal with those organic compounds of concern identified through a source survey and analysis. The process alternatives can be used alone or in combination with other unit processes in order to achieve the reduction of the particular organic chemicals. It is important to investigate the processes available, for different water qualities, by means of bench-scale, pilot-scale and plant-scale studies. Only through such studies we will be able to determine which processes are applicable to certain waters and which processes offer a broad spectrum of treatment for the removal of organic chemicals from our drinking water.

Scientists have been charged with irresponsibility for commenting with alarmist-type reports prior to a full study of highly technical work and its long term public impact. It is therefore important that time is taken to investigate both the concerns and the treatment options thoroughly. In this way it should be possible to arrive at

a proper and reasonable assessment of the situation; this hopefully will be the optimum solution.

In many cases we do not have the tools to answer the fears of consumers nearly as quickly as we would wish and some way of communicating the need for time to answer the questions must be found. Responsible reporting would further this need, and in addition, the credibility of scientists and those in positions of authority, which has been sorely strained in recent years would be enhanced. Thus it must be stressed that in the long term it is probable that the most reasonable solutions both from a practical and economic view-point will be obtained if the problem is investigated in a logical manner.

BIBLIOGRAPHY

1. Nicholson, A.A. et al; "Organics in Ontario Drinking Water, Part II, Ontario Ministry of the Environment, (April, 1977).
2. Symons, J.M.; Bellar, T.A.; Carswell, J.K.; Demarco, J.; Kropf, K.L.; Krobeck, G.G.; Seeger, D.R.; Slocum, C.J.; Smith, B.L., and Stevens, A.A., "National Organics Reconnaissance Survey for Halogenated Organics", JAWWA, 67: 634, (1975).
3. National Organics Monitoring Survey (NOMS). Technical Support Division, Office of Drinking Water, US EPA (1979).
4. Page, T.; Harris, R.H., and Epstein, S.S., "Drinking Water and Cancer Mortality in Louisiana", Science, 193:55, (1976).
5. Guidelines for Canadian Drinking Water Quality, 1978; Health and Welfare Canada (1979).
6. U.S. Federal Register, 43: No. 28, 5756-5780, (Feb. 9, 1978).
7. Tardiff, R.G., "Health Effects of Organics: Risk and Hazard Assessment of Ingested Chloroform", JAWWA, 69: 12, 658 (Dec. 1977).
8. Symons, J.M., "Utilization of Various Water Treatment Unit Processes and Treatment Modification for Trihalomethane Control", Proc. Control of Organic Chemical Contaminants in Drinking Water. Seminars sponsored by The Office of Drinking Water, U.S. EPA, Jan, 1980.
9. Trussell, R.R., and Trussell, A.R., "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies". JAWWA, 72:458 (Aug. 1980).
10. Rook, J.J., "Production of Potable Water from a Highly Polluted River", Water Treatment and Examination, 21: pt. 3, 259 (1972).
11. "Drinking Water Detoxification", Bk. Ed., Gillies, M.T., Noyes Data Corporation, Park Ridge, New Jersey, U.S.A. 1978.
12. "Drinking Water and Health", pub. National Academy of Sciences, Washington, D.C. June, 1971.
13. Bellar, T.A.; Lichtenberg, J.J., and Kroner, R.C. "The Occurrence of Organohalides in Chlorinated Water", JAWWA, 66:12:703 (Dec. 1974).
14. Symons, J.M., "Summary of Granular Activated Carbon Practise Data", Water Supply Research Division U.S. EPA, Cincinnati, Ohio, (Feb. 17, 1976).

15. Trussell, R.R., and Umphres, M.D., "The Formation of Trihalomethanes", JAWWA 70: 11: 604 (Nov. 1978).
16. Symons, J.M., and Stevens, A.A., "Physical-Chemical Treatment for the Removal of Precursors", Conference; Karlsruhe, Germany, (Sept. 1978).
17. Fung, M.C., "Reduction of Haloforms in Drinking Water Supplies", Ontario Ministry of the Environment Research Report, #69, (Sept. 1978).
18. Butterfield, C.T., and Wattie, E., "Relative Resistance of *E. coli* and *E. typhosa* to Chlorine and Chloramines", Pub. Health Reports, 59, 1661 (1944).
19. McCarty, P; Reinhardt, M., and Argo, D., "Organics Removal from Advanced Wastewater Treatment", Proc. 97th AWWA Annual Conference, Anaheim, California, (1977).
20. Singley, J.E.; Ervin, A.L.; Mangone, M.A.; Allan, J.M., and Land, H.H., "Trace Organics Removal by Air Stripping", AWWA Research Foundation Report, May, 1980.

ORGANIC CONTAMINANT REMOVAL
IN DRINKING WATER - FIELD EXPERIENCES

By:

R.B. Hunsinger

Ministry of the Environment,
Province of Ontario,
Technology Transfer Conference, No. 1,
Tuesday, November 25, 1980.
Skyline Hotel - Toronto

Dealing with micro-contaminants in drinking water involves four basic steps:

- 1) Risk Assessment - To ascertain if the contaminant represents a problem and how much hazard is involved,
- 2) Analysis Methods - To insure precise and accurate measurements of the contaminant in question,
- 3) Survey - To determine the source and extent of the contamination,
- 4) Removal Methods - To reduce or eliminate the contaminant if necessary. (1,2).

These four processes should theoretically be carried out in the order given, although in practice risk assessment is often not complete or even adequately begun, before it is necessary to move on a problem and explore the ramifications of a micro-contaminant in terms of analysis, survey and removal methods. Step one, risk assessment may be temporarily by-passed but the second phase of analysis methods is a pre-requisite step to proceeding to a survey or any study of removal methods.

Assessment of analytical methods is a most difficult problem for the water treatment engineer. Most of the chemistry involved is highly technical, experimental in nature, and has not been around for sufficient time to be examined even by the analytical scientific community. The first criteria in dealing with contaminants is to ascertain that accurate and precise measurement is possible. To cite an example of the type of problem that can emerge: In Ontario Asbestos Studies, the data gathered in 1972 for asbestos in water caused alarm with reported levels as high as 25-40 million fibres/litre. The only valid statement that can be made today regarding these figures is that there was fibrous material in the samples. Qualification, let alone quantification is not possible.

One method which has been used with some success in terms of method selection is the setting up of a committee of experts to

examine the various methods available and reach some consensus as to the most viable method and how the various methods compare. This is not a quick process but a sound analytical base is essential prior to any detailed problem investigation. The committee ideally should include analysts from industry, government and universities and it should be the aim of such a committee to compare various methods available by experimental means and inter-laboratory comparisons and in the end to reach some general agreement as to which method to recommend as a standard. The publication of such a method also affords those analysts who might object, the opportunity to formally disagree and possibly open further dialogue. The committee should also have an on-going function of analytical method revisions as new information comes to light. Very few methods stay static for any amount of time but the changes should be carried out in a unified industry-wide manner.

It can not be strongly enough stressed that we must have a reliable standardized method of measurement for any new or exotic contaminant in water as a first step to any program of monitoring or research on removal. Further, method development must be a separate and primary function and not part of surveys of drinking water. The water that our customers consume is much too important and emotional an issue to give out information based on half-baked ideas or hypothesis.

Examination of methods of analysis for trihalomethanes (THM) would show that the Purge & Trap method (3) as developed by the EPA is becoming the industry standard and is the method of analysis on which most trihalomethane regulations are based including the Guidelines for Canadian Drinking Water Quality (4) as well as the about to be published, Ontario Drinking Water Objectives (5).

Chloroform represents approximately 90% of the THM's found in water and as the reaction for the other trihalomethanes is similar in form, but varies quantitatively we shall deal with chloroform only in the discussion of methods of analysis. The Purge & Trap measures the purgeable or free chloroform.

The MOE laboratories have the capability to do the Purge & Trap method but prefer and routinely use the Direct Aqueous Injection Method or DAI method for THM which is a method developed by Meresz & Nicholson of the MOE (6,7). The DAI has the advantage of being much less expensive and a faster form of analysis. The DAI method produces chloroform results that are 1.5 to 2.2 times as high as those produced by the Purge & Trap method and thus overestimates the amount of free chloroform present. The explanation for this is that chlorination of natural waters causes the formation of certain non-purgeable intermediates that decompose within the gas chromatograph injection port to produce additional chloroform. Hence, the DAI is measuring not only the purgeable free chloroform but also a certain portion of the non-purgeable intermediates which have been converted to chloroform in the analysis process. The amount of intermediates converted to chloroform is site specific, but a fairly consistent DAI/free chloroform ratio can be developed. In the Belleville study, the ratio was determined to be 1.9/1. The conversion of intermediates is also a function of the design of the gas chromatograph used (8,9).

The DAI always produces numbers that are an overestimation of the free THM and thus is an excellent survey analytical method as it readily flags the areas of concern and has the advantages of being inexpensive and fast and thus allows survey programs that are more extensive than would be allowed by the Purge & Trap given the same monetary input.

When a survey location is flagged as approaching the limit for trihalomethanes, Purge & Trap analysis can commence to insure compliance with the limit. Many locations in Ontario have DAI levels in the range of 10 $\mu\text{g/L}$ which would translate to 7.5 $\mu\text{g/L}$, free trihalomethanes (10) and it is a waste to use an expensive, accurate, analytical tool to insure compliance with a limit of 350 $\mu\text{g/L}$. Further, the numbers produced by the DAI are comparable over the long term for any given site.

There have been about 700 organics identified in drinking water with the use of gas chromatograph-mass spectroscopy (GC/MS) and more are being added frequently.

When the Brantford Project was begun in 1978, an attempt was made to develop an organic scan using a GC/MS in which a graphical presentation of the organics present in the water albeit in an unidentified and unquantified form, would be available. In this manner it would be possible to compare general organic removal across a process and possibly identify and quantify substances of interest. This work was attempted based on the findings of Grob & Grob (11). Although the method was tested extensively by a contractor at the University of Western Ontario, it was found to be too cumbersome given the present state-of-the-art and the project was finally abandoned. A current Research Advisory Committee project is investigating this further.

As noted above, specific organic measurements are expensive, difficult and sometimes not even possible, so the use of surrogate organic measurements has become a much sought after panacea. Surrogates include such things as:

TOC	-	Total Organic Carbon
DOC	-	Dissolved Organic Carbon
TOX	-	Total Organic Halogen
TOCl	-	Total organic chlorine
UV	-	Ultraviolet (Extinction @ 254)

TOC is the most common organic surrogate seen in the literature. MOE uses a DOC which is similar to the TOC but does not measure the particulates.

These surrogates are extremely useful measurements but are analytical method specific and vary greatly from laboratory to laboratory and thus in many cases, are not directly comparable and are in need of standardization.

As mentioned above, a survey may begin before risk has been thoroughly assessed but analytical method development must be a prerequisite to any further work. This was in fact the case for trihalomethanes in that the DAI method was in place at the survey commencement. The risk assessment for THM has been much harder to come by, in that approximately 6 years after the commencement of the survey, we are about to have published for Ontario, a THM limit of 350 $\mu\text{g}/\text{L}$. This limit is based on the same risk information on which EPA derived their limit of 100 $\mu\text{g}/\text{L}$. Both limits refer to free or purgeable THM but the U.S. limit is based on averages over time whereas the Ontario limit is based on a single occurrence exceeding the limit.

A survey for the purpose of monitoring THM in Ontario was initiated in 1974 with 29 municipalities and has gradually been increased to the point that in 1980, there are 132 municipalities being monitored.

The general rationale behind the selection of the municipalities to be monitored first was a combination of probable occurrences based on humic content of the surface water, population size and also representative samples from the various watersheds.

The most up-to-date results of the survey for chloroform in Ontario are presented in Table 1 (10).

TABLE 1

DAI CHLOROFORM LEVELS IN ONTARIO DRINKING
WATER SURVEY 1980

<u>Chloroform Level</u>	<u>Number of Locations</u>
0 - 100 $\mu\text{g}/\text{L}$	62 (57%)
100 - 200 "	25 (23%)
200 - 300 "	13 (12%)
300 - 400 "	6 (6%)
400 - up "	2 (2%)

As can be seen, about 80% of the locations have chloroform below 200 $\mu\text{g/L}$. Considering that chloroform represents 90% of total THM and also that the DAI is measuring about 1.5 - 2.2 times the Purge & Trap, then 80% of the locations in Ontario presently being monitored, (which are considered to be the locations with the highest probability of THM occurrence) are below 100-150 $\mu\text{g/L}$ free THM. Eighty percent of the locations examined have THM maximums below 50% of the proposed limit.

Of the remaining 20% of the locations those approaching the limit would be switched to a monitoring program based on Purge & Trap to better assess the situation or at the least a Purge & Trap-DAI comparison would be done in order to establish a ratio.

After the establishment of this more accurate monitoring, the next step would then be to attempt to identify the cause of the high THM levels, and lastly determine suitable design and operating measures for reducing these substances, while ensuring that adequate disinfection is maintained.

In terms of removal methods, an extensive in-house MOE program on removal was carried out. Further, the Research Advisory Committee has sponsored two organic removal projects; one in Belleville and one in Brantford. Complete descriptions of the activities of these programs are beyond the scope of this paper, but specific areas from each are described below in order to illustrate the nature of the field experiences with the removal of organic contaminants.

Bench-scale studies at MOE by Fung (12) were begun in the mid 70's to determine the effectiveness of reducing the chloroform precursors prior to their conversion to chloroform. This process assumes the use of post-chlorination. This study examined effectiveness of:

- 1) coagulation utilizing various types of coagulants and coagulant aids,

- 2) adsorption on granular activated carbon (GAC),
- 3) the use of powdered activated carbon (PAC).

Results of the research studies on the reduction of precursors shows that:-

- 1) substitution of post-chlorination for pre-chlorination generally decreased the amount of haloform in the effluent by 50% in any given process configuration,
- 2) Using post-chlorination, the efficiency of alum used alone was about 44%. With the addition of activated silica, the efficiency was increased to about 90%,
- 3) Reduction of haloform precursors was not significant when using PAC at a generally accepted rate,
- 4) GAC was found to be effective in reducing haloform precursors up to 90% regardless of the pre-treatment processes,
- 5) Ozone, potassium permanganate and hydrogen peroxide were tested as possible alternate oxidants to chlorine in the pre-treatment processes and did not affect the performance of the subsequent coagulation in reducing chloroform precursors.

The Belleville project funded by the Provincial Lottery was carried out by the Belleville P.U.C. and Gore & Storrie Consulting Engineers (13). This was a full-scale project designed to ascertain the effects of moving the chlorination from one end of the process to the other. No alternate method of disinfection was being used at the head of the process.

The primary objective was to determine what effect this discontinuation of pre-chlorination would have on the following:

- I) the removal of precursor organic compounds and the resultant change in THM levels with chlorination applied after the coagulation, settling and filtration processes,

- II) The quality of the finished water in terms of parameters such as taste and odour, turbidity and colour,
- III) Plant operations and water production.

The problems anticipated as a result of the discontinuation of pre-chlorination were:

- I) possible taste and odour increase to processed water in the settling tanks imparted by unchlorinated settled material,
- II) possible biological growths in the filters resulting in shorter filter runs and degraded filtered water quality.

The plant was split for this project with a small portion of the flow going through coagulation, flocculation, sedimentation and filtration and then on to post-chlorination. The post-chlorinated water was sent to waste due to the experimental nature of the treatment.

In terms of objective II, namely the effect on other parameters such as taste and odour, colour, turbidity, etc., the average values for the specific parameters as well as a percent reduction through the process for the 9 month period from February to October covering both cold and warm water conditions show very little difference between the pre-chlorinated and post-chlorinated streams for turbidity, colour, taste and odour.

Similarly, the altered water quality going onto the filters did not negatively effect the headloss. In fact, a slight improvement was noted in the post-chlorination stream. Physical examination of the filter media and filter walls showed no biological growths or other unusual accumulation of material.

Comparison of the results obtained for the two methods of plant operation, experimental (post-chlorination) and normal (pre-chlorination), shows virtually no difference in the levels of chloroform and THM's present in both settled and filtered water samples. During the February to October time span, the average values

for chloroform in water after filtration were 104 $\mu\text{g}/\text{L}$ (post-chlorination) and 102 $\mu\text{g}/\text{L}$ (pre-chlorination). Both methods did achieve some improvement in chloroform and THM levels as compared with chlorinated raw water samples, indicating that the coagulation and settling process does remove some precursors and THM.

The average reduction in THMs across the flocculation and settling phases of the plant process were between 13% and 15%.

Work reported by Love et al (14) and Fung (12) in the MOE bench scale studies suggests an expected reduction in trihalomethanes in the range of 50% due to the moving of the chlorination point. This was not the case in the Belleville water. This is becoming a recurring theme when dealing with organic removal. The broad spectrum solution does not seem to be applicable, rather, we find ourselves having to examine many possible processes in each specific case.

R.A.G. Simmons (15) reported to AWWA in 1980 on further work carried out at Belleville under Lottery Funding. The bench-scale work consisted of chlorinating the raw water for a given time to achieve a given level of disinfection (500 colonies/100 ml total bacteria count). Following the achievement of this level of disinfection, the water was then chemically dechlorinated to 0 and then rechlorinated to 0.75 and 1.5 mg/L . Simmons states that a chlorine dosage of 4.5 mg/L for a contact time of 25 minutes, necessary to achieve the 500 colonies/100 ml bacteria criteria, then dechlorinated/rechlorinated to 0.75 and 1.5 mg/L produced 142 $\mu\text{g}/\text{L}$ & 205 $\mu\text{g}/\text{L}$ of chloroform respectively after 24-hours contact time. A similar dosage of 4.5 allowed to stand in a control sample for 24 hours produced 275 $\mu\text{g}/\text{L}$ chloroform. The paper goes on to develop the scenario to include costs and operational variables. Although dramatic, the results are based on limited bench-scale experiments; future research may look at this scheme further.

The Brantford project is a pilot plant operation; the main purpose of which is to test the effect of GAC on the removal of THM precursors and

other organic compounds from the water prior to chlorination. This project goes one stage further than the Belleville experiments in that it is not only testing post-chlorination but is also going to determine the effects on chlorinated organics of substituting GAC for the anthracite in the present filter beds. As with any other modification the status quo must be maintained in terms of other treatment parameters. For example, Brantford is now using PAC for taste and odour removal and thus the GAC must be able to maintain the taste and odour control as well as remove the organic precursors. Further, the adequacy of disinfection must be maintained. The Brantford project is also being funded under the Provincial Lottery system and is being operated by the City of Brantford Public Utilities Commission under the direction of K. Edwards.

Fundamental information in regards to the behaviour of the organic contaminants is often not fully developed and hence much time is spent on doing fundamental research. This has been evident at both Belleville and Brantford. As an example, at Brantford, erratic results were being obtained in terms of the trihalomethane results from the pilot plant using a standard chlorine dosage. Conventional thought as noted by Stevens and Symons (16) was that given a free chlorine residual the maximum amount of chloroform would develop. At Brantford this was shown not to be the case (17). After considerable work it was determined that the maximum formation did not occur until well past the point of a free chlorine residual. The chloroform production does not level out until 30 mg/L free chlorine residual has been applied. Part of this may be a function of the DAI measurement and this is still to be investigated. Full discussion of this phenomenon will be presented in the Brantford report but suffice to say that fundamental problems such as this, make assessment of complex removal methods very difficult.

The Brantford Project has attempted to assess the practicality of GAC in a retrofit situation in which major plant modifications

would not be necessary. The raw pilot plant data to date would suggest that the carbon in the filter would require regeneration in the neighbourhood of 3-40 days depending on the criteria of exhaustion used. Modifications to the front end of the pilot plant are now being assessed to lengthen the carbon life.

In summation, an approach to dealing with contaminants has been outlined that includes:

- 1) Assessment of risk,
- 2) Analysis of methods-review and standardization,
- 3) Survey to determine the extent of the contaminant,
- 4) Removal method to reduce or eliminate the contaminant if necessary.

The chlorinated organics are merely the very tip of the organics iceberg and it is extremely important that a standardized rational approach be developed to handle new and exotic organic pollutants as they emerge.

Dealing with the public concerns, having full technical information, avoids the problems of over extrapolation and misinterpretation which can happen when the brush-fire approach to dealing with micro-contaminants is taken.

REFERENCES

- 1) Hunsinger, R.B., Drinking Water Pollution by less Well Known Contaminants, paper presented at the AWWA Atlantic Section (1979).
- 2) Roberts, K.J., Assessment of Municipal Water Quality and MOE Requirements, paper presented at Urban Water Supply Conference, University of Toronto (1980).
- 3) The Analysis of Trihalomethanes in Finished Waters by the Purge & Trap Method, Method 501.1. US EPA Cincinnati, Ohio (1979).
- 4) Guidelines for Canadian Drinking Water Quality, 1978. Health and Welfare, Canada (1980).
- 5) Ontario Drinking Water Objectives, 1980. Ontario Ministry of the Environment, Toronto (in press).
- 6) Nicholson, A.A., Meresz, O., Organics in Ontario Drinking Waters, Part I, paper presented at the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy (1976).
- 7) Smillie, R.D., Nicholson, A.A., Meresz, O., Duholke, W.K., Rees, G.A.V., Roberts, K.J., Fung, M.C., Organics in Ontario Drinking Waters, Part II, Ontario Ministry of the Environment (1977).
- 8) Pfaender, F.K., Jonas, R.B., Stevens, A.A., Moore, L., Hass, J.R., J. Environ. Sci. Technol. 12, 438-441 (1978).
- 9) Peters, C.J., Young, R.J., Perry, R., J. Environ. Sci. Technol. 14, 1391-1395 (1981) .
- 10) Martin, G.W., Survey of Ontario Drinking Water for Haloforms, Ontario Ministry of the Environment (personal communication).
- 11) Schalekamp, M., Bakker, S.P., Effluent and Water Treat. J. January (1978).
- 12) Fung, M.C., Reduction of Haloforms in Drinking Water Supplies, Report #69, Ontario Ministry of the Environment (1978).
- 13) Simmons, R.A.G., "Chloroform Reduction Investigation Programme at Belleville Utilities Commission", Report to the Ontario Ministry of the Environment (1979).
- 14) Love, O.T., Carswell, J.K., Miltner, R.J., Symons, J.M. Treatment for the Prevention or Removal of Trihalomethanes in Drinking Water. Appendix 3 to "Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes", US EPA.

- 15) Simmons, R.A.G., "Chlorine - Disinfection Effectiveness and THM Control", paper presented at the AWWA Ontario Section meeting (1980).
- 16) Stevens, A.A., Symons, J.M., Formation and Measurement of Trihalomethanes in Drinking Water. Proceedings - Control of Organic Contaminants in Drinking Water - US EPA (1980).
- 17) Edwards, K.L., Oberski, D.G. Organic Contaminant Removal Trial of Granular Activated Carbon at City of Brantford Water Supply (in press).
- 18) Gillies, M.T., Drinking Water Detoxification, Noyes Data Corp. Park Ridge, New Jersey, U.S.A. (1978).

**Viruses and
the Environment**

- **Goff Jenkins**
Virology Scientist
Laboratory Services Branch
Ontario Ministry of the Environment

November, 1980.

Human and animal viruses are minute infectious agents that range in size from 20-250 nanometers. The typical virus particle consists of a nucleic acid core surrounded by a protein coat. Consequently, a virus particle in solution behaves as a polyelectrolyte, bearing a net positive charge at acidic pH's below its isoelectric point, and a net negative charge at pH's above its isoelectric point. This property is important in recovery methods for viruses. The virus particle adsorbs to charged surfaces under suitable conditions, and can subsequently be eluted.

A virus in the environment, for example, in sewage or water, behaves as a charged particle, adsorbing freely to particulate matter or to other viruses. This factor plays a major role in the removal of viruses during sewage treatment because adsorbed virus particles may be precipitated out and aggregated in the sludge.

Over one hundred different viruses are known to be excreted in human feces (1). A number of these viruses are resistant to conventional wastewater treatment plant procedures and are capable of remaining viable in water for long periods of time. Since a single infective virus particle may be capable of inducing infection and disease in a susceptible host, the presence of any viruses in a water supply poses a potential health hazard (2).

The viruses of prime concern, from an environmental viewpoint, are the enteric viruses. There are approximately 108 known enteric viruses (1) (Fig.1). These viruses are capable of multiplications within the gut, and may be excreted in concentrations as high as $10^9 - 10^{11}$ particles/g of human fecal material (3).

Documented syndromes that may be induced by enteric virus infections range in severity from colds, fever and diarrhea, to polio-like paralysis (1) (Fig. 2). A single type of virus can manifest itself in a variety of clinical symptoms, while the same symptoms can be produced by many different viruses. For example, aseptic meningitis may be induced by polioviruses, echoviruses, coxsackieviruses, and other enteroviruses.

FIG. 1 - ENTERIC VIRUSES OF HUMAN ORIGIN

<u>VIRUS GROUP</u>	<u>NUMBER KNOWN</u>
1. Enteroviruses	
Polioviruses	3
Echoviruses	31
Coxsackieviruses	29
Other	4
2. Adenoviruses	31
3. Reoviruses	3
4. Hepatitis A	1
5. Hepatitis B	1
6. Rotaviruses	1+
7. Others	4
TOTAL	≤ 108

FIG. 2 - SYNDROMES IN MAN CAUSED BY ENTERIC VIRUSES

ASEPTIC MENINGITIS
PARALYTIC POLIOMYELITIS
FEVER
COLDS
DIARRHEA
HERPANGINA
MYOCARDITIS
ACUTE RESPIRATORY DISEASE
PHARYNGO-CONJUNCTIVITIS
ACUTE HEMORRHAGIC CYSTITIS
HEPATITIS LIVER INVOLVEMENT
PARALYSIS (POLIO-LIKE)
RASH

It has been estimated that over 60% of all human diseases are of viral origin (4). What is not known is the percentage of viral diseases that are waterborne. For most virus infections, the source and route of infection can not be determined.

The epidemiology of waterborne viral outbreaks has been difficult to elucidate, because disease symptoms may take weeks to appear, and most infections are subclinical or asymptomatic. In addition, efficient methodologies for the isolation and identification of the viruses of prime concern, namely the hepatitis A virus, the rotaviruses, and the Norwalk agent, have not been developed as yet.

The Centre for Disease Control in Atlanta, in 1976, reported that the average annual number of waterborne disease outbreaks (including viral and bacterial outbreaks) is increasing (Fig. 3) (9). Although only one-third of the known enteric viruses can be cultivated in vitro, much of the increase shown in Fig. 3 is due to improved detection methods for enteric viruses.

Eighty-three hepatitis A outbreaks, attributable to drinking water, were reported in two papers published in 1967 and 1976 (5, 6). Numerous other waterborne outbreaks of "infectious hepatitis" have been documented in the literature (7, 8). When a comparison is made between the annual incidence of hepatitis A and typhoid fever in the United States from 1952 to 1972 (Fig. 4), it is evident that the number of cases of the bacterial disease, typhoid fever, has decreased with improved water treatment practices, whereas the number of cases of hepatitis A appears to be increasing (10).

The most common human infection associated with a waterborne agent is nonbacterial gastroenteritis (11). The agents responsible for these infections will probably be shown to be viruses. Rotavirus, a recently discovered enteric virus, has been established as the major pathogen of nonbacterial infantile diarrhea throughout the world. Up to 10^{11} Rotavirus particles/g of feces may be excreted by an infected individual. Laboratories world-wide are currently involved

FIG. 3 - AVERAGE ANNUAL NUMBER WATERBORNE DISEASE OUTBREAKS (IN UNITED STATES)

1938-1975

AVERAGE ANNUAL NUMBER

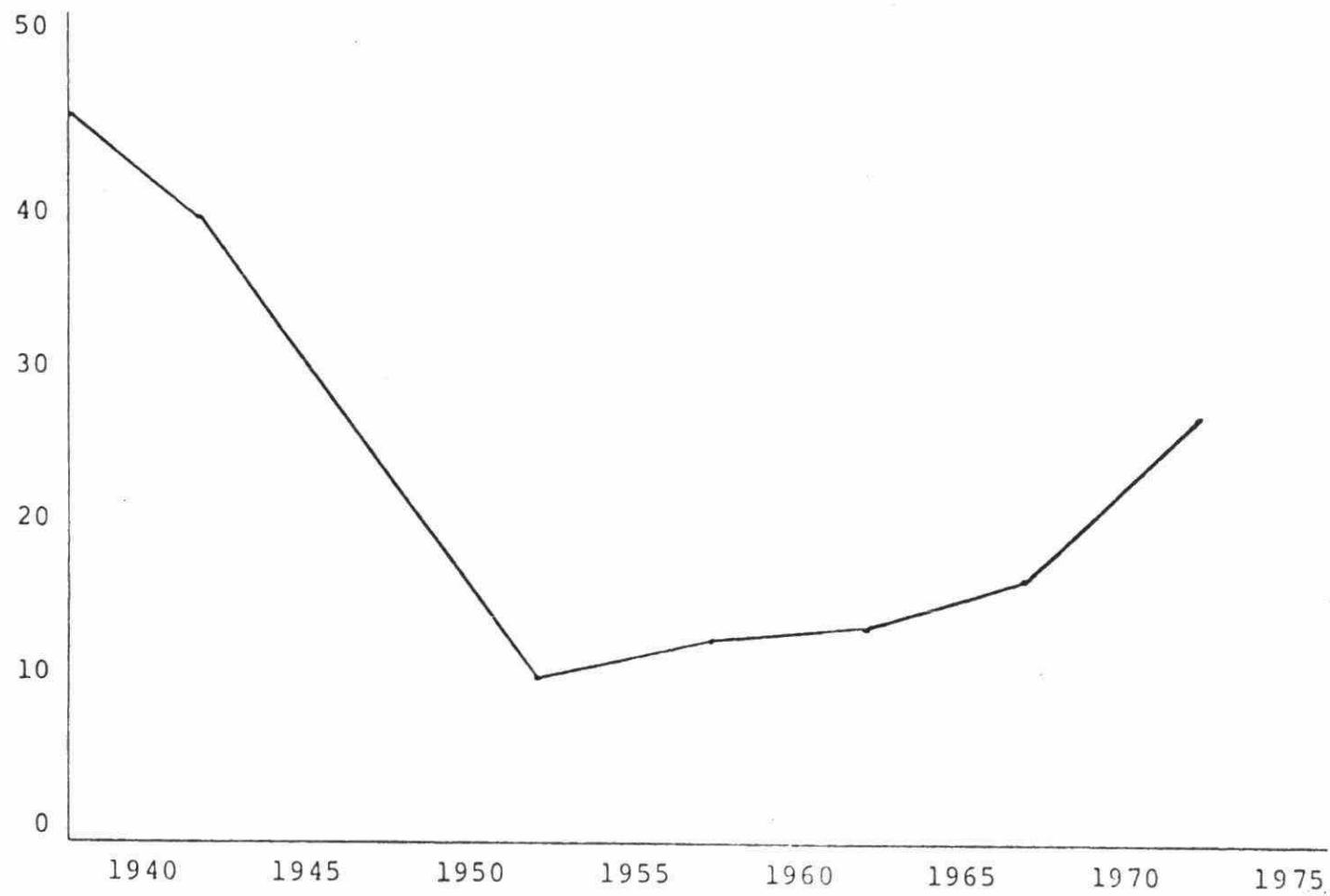
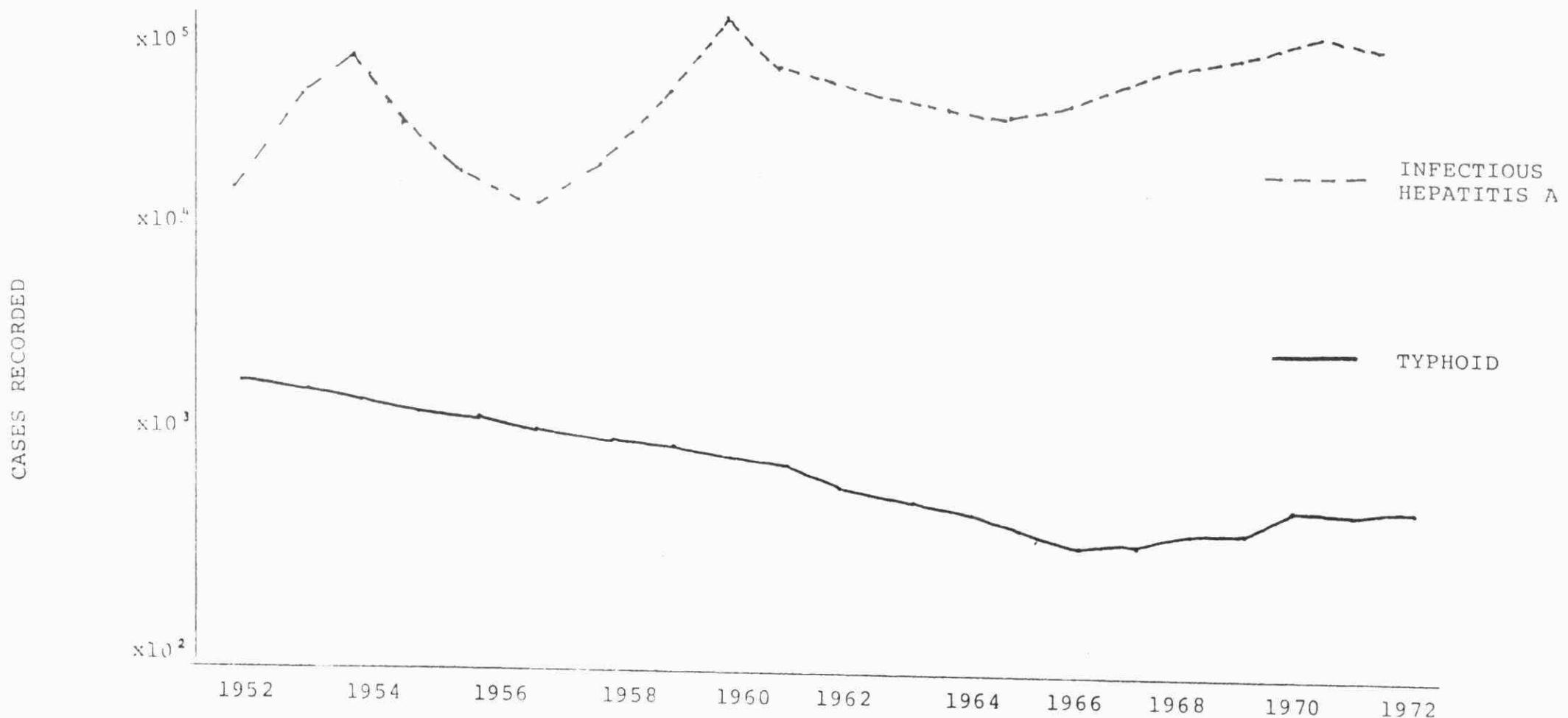


FIG. 4 - ANNUAL INCIDENCES OF INFECTIOUS HEPATITIS AND TYPHOID FEVER IN THE U.S. 1952-1972.



in the development of methods for the routine isolation and identification of human rotaviruses from the environment. The need for such a methodology was re-emphasized at the 1980 International Viruses and Wastewater Treatment Conference in England. A study by Cabelli on the incidence of swimming-associated gastrointestinal infection showed that a significant level of infection was incurred by swimmers in waters which were well within microbiological standards for body-contact recreation (12). The evidence presented suggested that rotaviruses could be the causative agent, but the virus was not isolated.

In addition to the enteric viruses discussed so far, numerous others are of major concern. The enteroviruses, which include poliovirus, coxsackievirus and echovirus are excreted in substantial numbers in the feces of infected individuals for varying periods of time, with a mean duration of excretion for poliovirus of 50 days.

It is now well documented that enteric viruses are capable of surviving standard sewage treatment processes and consequently may be released into the water through sewage effluents (13). The different stages of sewage treatment vary in their efficiency for their removal and/or inactivation of viruses (Fig. 5).

A) Primary Sedimentation

Since viruses in water are often associated with particulate matter, a number of them may be precipitated out during primary sedimentation. The removal rate is highly variable and the viruses may remain viable in the sediment.

B) Biological Treatment

Activated sludge treatment, trickling filters, and waste stabilization ponds vary greatly in removal efficiency. Under ideal conditions, activated sludge treatment is very efficient for the removal of most enteric viruses. However the variability of the environmental conditions present during activated sludge treatment, in many cases results in a greatly reduced virucidal activity. Trickling filters and stabilization ponds are even more erratic in their virus removal and inactivation efficiencies.

FIG. 5 - VIRUS ELIMINATING EFFICIENCY OF VARIOUS STAGES
OF SEWAGE AND WATER TREATMENT

TYPE OF TREATMENT	REMOVAL EFFICIENCY	INACTIVATION EFFICIENCY
1. PRIMARY SEDIMENTATION	< 55%	NONE
2. BIOLOGICAL TREATMENT	0-99%	VERY POOR
3. TERTIARY TREATMENT	2-99%	VARIABLE
4. DISINFECTION	0-99%	0-99%

C) Tertiary Treatment

Tertiary treatment is effective for the removal of viruses. It is capable of removing 99.999% of all viruses under ideal conditions. However the virus particles may remain viable and accumulate in the sludge, and consequently remain a hazard.

The addition of lime to raise the pH of sewage sludge to between 11.0 and 11.5 has been found efficient for the removal and inactivation of enteric viruses (14). This procedure was used at the Woodstock sewage treatment plant to prevent the spread of polioviruses during the poliomyelitis outbreak in 1978.

D) Disinfection

Traditionally, chlorination has been the major means of disinfection in North America. The virucidal action of chlorine is dependent upon such factors as the chemical nature, pH, and temperature of the material being treated. Large amounts of organic matter are present in the effluents from activated sludge plants. Consequently, large reductions of infectious viruses are not attained because of the combination of the chlorine with ammonia and organics. Further complicating the problem is the wide variability in resistance of different enteric viruses to inactivation by chlorine. In a study of the resistance of 25 human enteric viruses with 0.5 mg free chlorine residual, the time required for 99.99% inactivation varied from two minutes to two hours (15). Viral susceptibility to inactivation by chlorination is pH dependent, and the pH of sewage effluents is not optimal for virucidal inactivation. As mentioned earlier, virus particles in solution act as charged particles. Virus particles may aggregate and become adsorbed to particulate matter. It has been shown that adsorbed virus particles are much more resistant to inactivation by chlorination than are unassociated particles. Consequently, the efficiency of chlorination is minimized even further.

In summary, virus removal during sewage treatment is realized primarily through precipitation of the virus particle, and chlorine disinfection, as practised, is not efficient for the production of a safe virus-free effluent.

There is a growing concern about the potential health hazard posed by viruses in the environment. The need to assess this risk has become readily apparent in recent years.

In a study supported by Provincial Lottery funds, Dr. Sattar in Ottawa developed the talc-celite procedure for the recovery of pathogenic human viruses from potable and surface waters (16). In phase I of his study, Dr. Sattar detected the presence of enteric viruses in 100% of all raw sewage samples, and in greater than 50% of chlorinated effluents and water samples collected at Britannia Beach (Fig. 6) (17). Forty percent of the samples of raw water collected at a Water Purification Plant were positive for enteric viruses. In addition, 9 out of 35 potable water samples exhibited evidence of transmissible cytopathic degeneration in tissue culture. The detection of morphological changes or cytopathic effect (C.P.E.) in tissue culture, is the first stage in isolating and identifying viruses. C.P.E.'s however may be caused by agents other than viruses, such as mycoplasma, or they may be caused by toxic factors. Therefore the presence of viruses must be confirmed by electron microscopy or serological techniques. The C.P.E. in these nine samples was transmissible, indicating the C.P.E. was not due to toxic factors, but no virus particles could be detected under the electron microscope. This does not rule out the possibility of a viral etiology.

In phase II of the study, Dr. Sattar analyzed samples from a Water Purification Plant, and from the Ottawa River, downstream of the Gatineau and Rideau Rivers (18). All 76 river samples were positive for virus, and 29% (11 of 38) treated water samples from the Water Purification Plant showed C.P.E.'s Preliminary electron microscopy showed the presence of virus-like particles. These data indicate the need to assess the risk associated with the presence of pathogenic viruses in potable waters.

FIG. 6 - RESULTS OF VIROLOGICAL TESTING FROM THE
OTTAWA RIVER STUDY

<u>SAMPLE TYPE</u>	<u>NUMBER OF SAMPLES</u>	<u>NUMBER OF SAMPLES-POSITIVE*</u>
SEWAGE TREATMENT PLANT		
a) RAW SEWAGE	23	23
b) CHLORINATED EFFLUENT	24	13
OTTAWA RIVER	76	76
BEACH	43	28
WATER PURIFICATION PLANT		
a) RAW WATER	59	39
b) TREATED WATER	63	11**
c) TAP WATER	10	0***

* POSITIVE - BY C.P.E. AND ELECTRON MICROSCOPY.

** - OTHER SAMPLES SHOWED C.P.E. - NOT CONFIRMED BY E.M.

*** - ONE SAMPLE EXHIBITED C.P.E. - NOT CONFIRMED BY E.M.

The Ontario Ministry of the Environment has developed the capacity to perform environmental virological analyses, and is currently participating with the University of Toronto in an epidemiological study of selected bathing sites in Southern Ontario. A portion of this study is being supported by Provincial Lottery funds.

In the first phase of this study, which was completed in the spring of 1980, selected bathing beach sites were sampled and analyzed for the presence of enteric viruses. A sewage treatment plant and its receiving waters in Southwestern Ontario were also examined. The first set of samples from the S.T.P. was collected in December 1979, while the plant was taking part in a chlorination study and the chlorination was shut off. The second set of samples was collected from the chlorinated effluent in mid-January, 1980.

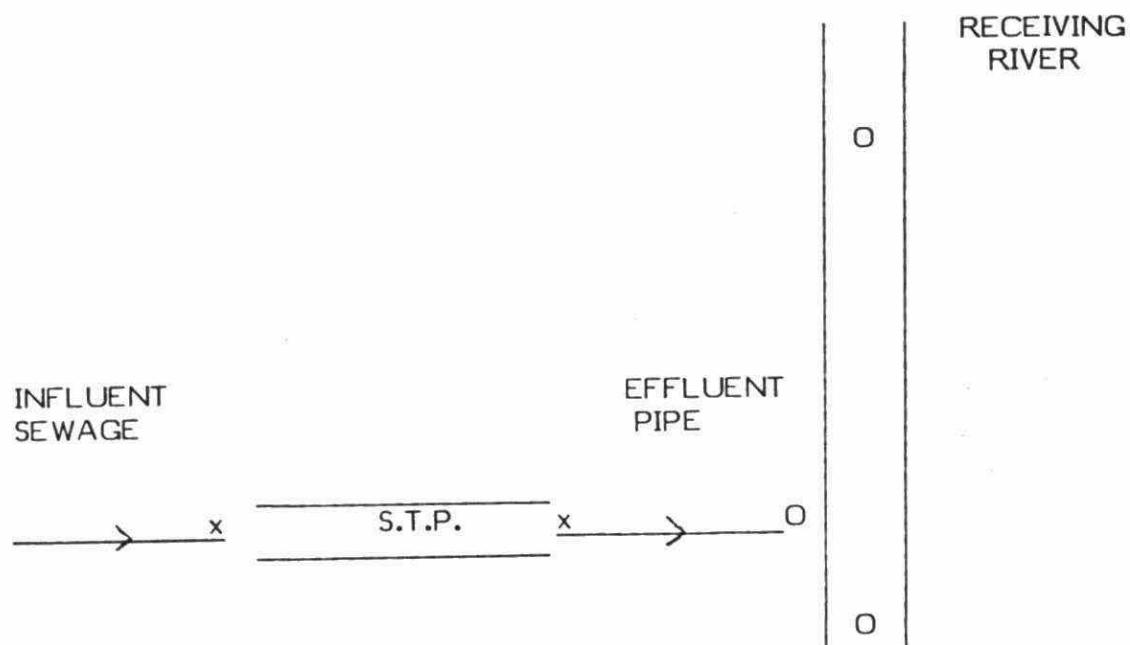
Five samples were collected at the sewage treatment plant during each survey (Fig. 7). Sewage pad samples were collected from the influent sewage line, and from the S.T.P. effluent after the chlorine contact chamber and before the effluent pipe. Forty litre grab samples were collected from the discharge end of the effluent pipe, and from the receiving waters upstream and downstream from the discharge.

The electron microscopic identification of the virus isolates was carried out by the Electron Microscopy Department of the University of Toronto and the Water Quality section of the Ministry of the Environment.

Twenty-two beach-site samples were analyzed in the first stage of the study. Viruses were not detected in any of the samples. However, all ten samples collected from the sewage treatment plant and the receiving waters were positive for viral cytopathic effects on tissue culture (Fig. 8).

While the chlorination was shut off, enterovirus particles were recovered from the influent pad sample and the effluent grab sample. Reovirus particles were recovered from the effluent pad sample, and the upstream and downstream receiving water samples (Fig. 9).

FIG. 7 - SEWAGE TREATMENT PLANT SAMPLING



x = SAMPLING LOCATION (SEWAGE PAD)

O = SAMPLING LOCATION (40 L. GRAB)

FIG. 8 - RESULTS OF SAMPLING

<u>SAMPLE TYPE</u>	<u>NUMBER OF SAMPLES</u>	<u>NUMBER POSITIVE</u>
SURFACE WATER (BEACH)	11	0
SEDIMENT (BEACH)	11	0
SEWAGE PAD	4	4
SEWAGE EFFLUENT (GRAB SAMPLE)	2	2
SURFACE WATER (RIVER)	4	4

FIG. 9 - RESULTS OF SEWAGE TREATMENT PLANT SAMPLINGA. CHLORINATION OFF

SAMPLE TYPE	CELL CULTURE DIAGNOSIS	E.M. IDENTIFICATION
SEWAGE INFLUENT (PAD)	+	ENTEROVIRUS
SEWAGE EFFLUENT (PAD)	+	REOVIRUS
SEWAGE EFFLUENT (GRAB)	+	ENTEROVIRUS
RECEIVING WATER - UPSTREAM	+	REOVIRUS
RECEIVING WATER - DOWNSTREAM	+	REOVIRUS

All five samples collected at the sewage treatment plant with chlorine disinfection in operation were also positive for viral cytopathic effects in tissue culture (Fig. 10). Electron microscopic and serological identification has not been completed on these isolates.

In the second phase of the study carried out during the summer of 1980, seventy-seven samples from selected bathing beaches, recreational waters, and sewage treatment plants were analyzed for the presence of enteric viruses. Sewage Treatment Plants in St. Catharines, Toronto, and Port Hope, beaches in St. Catharines and Wasaga, and selected conservation areas were sampled. First passages have been completed on all samples. Evidence of viral presence is evident in several samples, and confirmation through E.M. and serological techniques is currently underway.

Concurrent with the epidemiological study, the M.O.E. virus laboratory is constantly refining the procedures used for recovering enteric viruses. We are currently assessing automated sampling and processing equipment as described by Dr. Payment (19). The use of positively charged cartridge filters with improved virus adsorption capacity as described by Sobsey are being evaluated (20). Standard methods for virological analyses should be established within two years.

We are also establishing the capacity to analyze potable water samples. The talc-celite method of Dr. Sattar will be one of the systems evaluated. Drinking water sample processing must be automated and of a continuous flow type due to the large sample volume, 1000 litres.

It now appears likely that rotaviruses will be found to have a waterborne etiology, and the significance of this will be understood when the incidence of rotavirus infection in the population can be properly assessed. If, as Cabelli suggests, rotaviruses turn out to be the prime agent involved with swimming-associated gastrointestinal infection, it becomes essential to develop the capacity to recover rotaviruses from the environment and cultivate them in vitro so this risk may be properly assessed.

FIG. 10 - RESULTS OF SEWAGE TREATMENT PLANT SAMPLINGB. CHLORINATION ON

SAMPLE	CELL CULTURE DIAGNOSIS	E.M. IDENTIFICATION
SEWAGE INFLUENT (PAD)	+	N.D.
SEWAGE EFFLUENT (PAD)	+	N.D.
SEWAGE EFFLUENT (GRAB)	+	N.D.
RECEIVING WATER -UPSTREAM	+	N.D.
RECEIVING WATER - DOWNSTREAM	+	N.D.

As the procedures for recovering enteric viruses are improved and refined, they may be used to study the virus removing efficiency of selected sewage treatment plants. As stated earlier, chlorination, as normally practised, is inadequate for the generation of a safe effluent. Studies need to be done to establish the best means of producing a virus-free effluent.

Finally, studies need to be designed to properly assess the risk posed by the presence of viruses in the environment. The viruses of concern must be clearly identified, methods must be available or developed for their recovery from the environment, and epidemiological evidence should be gathered to ascertain what levels of virus pose significant health problems. Such epidemiological studies are complex and require a great deal of man power, but they are essential if we are to establish meaningful criteria for safe virus levels in recreational and/or potable waters.

Bibliography:

- 1) Melnick, J. L. (1978). "Water as a Reservoir of Virus in Nature and Means for Control", in *Viruses and Environment*, E. Kurstak and Karl Maramorosh (Eds.), New York. Academic Press, pp. 203-226.
- 2) Plotkin, S. A. and Katz, M. (1967). "Minimal infective doses of viruses for man by the oral route", in *Transmission of viruses by the water route*, G. Berg (Ed.), New York, John Wiley and Sons, pp. 151-166.
- 3) Editorial (1975), *Rotaviruses of man and animals, Lancet*, I, pp. 257-259.
- 4) Horsfall, F. L. (1965). "General Principles and Historical Aspects", in *Viral and Rickettsial Infection of Man*, F. L. Horsfall and I. Tamm (Eds.), Montreal: Lippincott Co., pp. 1-10.
- 5) Mosley, J. W. (1967). "Transmission of viruses by drinking water", in *Transmission of Viruses by the Water Route*, G. Berg (Ed.), New York: John Wiley and Sons, pp. 5-23.
- 6) Goldfield, M. (1976). "Epidemiological indicators for transmission of viruses by water", in *Viruses in Water*, G. Berg et. al. (Eds.), Washington, D.C.: Amer. Pub. Hlth. Assoc., pp. 70-85.
- 7) Bryan, J. A., Lehmann, J. D., Setiady, E. F. and Match, M. H. (1974). "An outbreak of hepatitis A associated with recreational lake water". *Amer. J. Epidemiol.* 99, 145-154.
- 8) Dennis, J. M. (1959). "1955-56 infectious hepatitis epidemic in Delhi, India", *J. Amer. Water Works Assoc.*, 51, pp. 1288.
- 9) Center for Disease Control (1976). *Food and Waterborne Disease Outbreaks: Annual Summary 1975*. U. S. Department of Health, Education and Welfare Publication No. (CDC) 76-8185.
- 10) McDermott, J. H. (1974). "Virus problems and their relation to water supplies", *J. Amer. Water Works Assoc.*, 66, pp. 693-698.

- 11) Sattar, S. A. (1978). *Viruses, Water and Health*. University of Ottawa Press. Ottawa, Ontario, Canada.
- 12) Cabelli, V. J. (1980). As reported at *Viruses and Wastewater Treatment, International Symposium*, Surrey, England. Sept. 15-17, 1980.
- 13) Berg, G. (1973). "Removal of viruses from sewage, effluents, and waters. 1. A review". *Bull. W.H.O.*, 49, pp. 451-460.
- 14) Sattar, S.A., Ramia, S. and Westwood, J. C. N. (1976). "Calcium hydroxide (lime) and the elimination of human pathogenic viruses from sewage. Studies with experimentally-contaminated (poliovirus, type 1, Sabin) and pilot plant samples.", *Can. J. Pub. Hlth.*, 67, pp. 221-226.
- 15) Liu, O. C. and McGowan, F. (1973). Effect of chlorination on human enteric viruses in partially treated water from the Potomac River estuary - Study report prepared for the U.S. Army Engineer Division, North Atlantic. Northeastern Water Supply Laboratory, Narragansett, R.I.
- 16) Sattar, S. A. and Westwood, J. C. N. (1976). "Comparison of talc-Celite and polyelectrolyte 60 in virus recovery from sewage: development of technique and experiments with poliovirus (type 1, Sabin) - contaminated multi-litre samples". *Can. J. Microbiol.*, 22, pp. 1620-1627.
- 17) Sattar, S. A. (1979). *Viral Pollution of the Ottawa River and its possible impact on the quality of potable and recreational waters in the Ottawa area - Phase II*. Final Report for the Ontario Ministry of the Environment Research Study Contract No. 77-004-11.
- 18) Sattar, S. A. (1978). *Viral Pollution of the Ottawa River and its possible impact on the quality of potable and recreational waters in the Ottawa area - Phase I*, M.O.E. Contract No. 77-004-11. University of Ottawa, Ottawa, Ontario.
- 19) Payment, P. and Trudel, M. (1980). "A simple low cost apparatus for conditioning large volumes of water for virological analysis", *Can. J. Microbiol.*, 26, pp. 548-550.

20) Sobsey, M.D. and Glass, J.S. (1980). "Poliovirus concentration from tap water with electropositive adsorbent filters", App. and Env. Microbiol., 40, 2, pp. 201-210.

BRUCE AND PICKERING
THERMAL PLUME
DEFINITION FLIGHTS

An Application of Thermal Sensing Techniques

by

Intertech Remote Sensing Ltd.

TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	
2.0 DATA ACQUISITION SYSTEM	
2.1 Sensor Platform	
2.2 Sensor	
2.3 Data Storage	
3.0 DATA PRODUCTION SYSTEM	
4.0 METHODOLOGY	
4.1 Fundamental Principles	
4.2 Thermal Infrared Linescanners	
4.3 Imaging and Processing	
4.4 Imagery	
5.0 CONCLUSIONS	

ABSTRACT

Intertech Remote Sensing Ltd., funded by a grant of the Provincial Lottery Trust Fund administered by the Ontario Ministry of the Environment provided airborne data acquisition services using an infrared linescanner to map the wintertime synoptic thermal plume characteristics off the Bruce Nuclear Power Development site on Lake Huron. In addition, Intertech acquired imagery of the waterborne thermal plume from the Pickering "A" N.G.S. site on Lake Ontario.

The imagery was acquired using a Daedalus Enterprises thermal infrared linescanner, equipped with a detector sensitive to emitted thermal radiation in the 8-14 micrometer portion of the electromagnetic spectrum. The output signals from the linescanner were recorded on an instrumentation tape recorder for subsequent laboratory processing.

1.0 INTRODUCTION

The imagery collected by an airborne thermal infrared linescanner represents surface radiation emitted from a scene as viewed by the scanner. The resulting thermal image is a two dimensional thermal display, with no depth information directly available to the investigator. The radiated energy viewed by the scanner is not only a function of the temperature of the scene, but is also affected by the emissivity characteristics of the material being viewed. Modern linescanners are capable of providing quantified data to the investigator by utilizing calibrated thermal reference sources as a benchmark to which the thermal content of the viewed scene is compared. Quantitative scanner temperatures are referred to as apparent surface temperatures. Additional procedures (not undertaken during the present study), including ground measurements and atmospheric modelling are required to convert image temperatures to absolute ground temperatures if required. Buoyant waterborne thermal plumes can be easily imaged by linescanners to provide synoptic information on plume shape, direction and areal extent.

2.0 DATA ACQUISITION SYSTEM

2.1 Sensor Platform

The sensor was installed in a twin engined, non pressurized modified Cessna 411. Intertech currently operates two aircraft with airborne infrared linescanners in Canada (Ottawa and Calgary).

2.2 Sensor

The sensor used was a single channel Daedalus Infrared Linescanner Model 1230, operating at a scan rate of 60 scans/second. The detector used was sensitive to radiation in the 8-14 micrometer portion of the electromagnetic spectrum and provided a spatial resolution of 1.7 milliradians (at nadir) and a thermal resolution of 0.2°C. The configuration of the scanner provided an across track field of view of 77.2° (unvignetted). The scanner was solidly attached to the airframe and corrected for instabilities in the roll axis of +/-5° from horizontal. The sensor was equipped with calibrated black body thermal reference sources.

2.3 Data Storage

The signals generated by the scanner were recorded on a Weston-Schlumberger Sangamo Sabre 6 instrumentation tape recorder, operating at a recording speed of 30 inches/second. The recording medium was Ampex 1" Magnetic Instrumentation tape.

3.0 DATA PRODUCTION SYSTEM

The hard copy imagery of the series of overflights was generated on the analogue processing facility of the Canada Centre of Remote Sensing in Ottawa. The processing facility consists of the following major components:

1. 3-M Mincom Instrumentation Tape Recorder
2. Daedalus 2 Channel Analogue Processor, Model 612
3. Daedalus Field Printer, Model 617

The output products consisted of 127 mm. wide format continuous roll film processed in two different modes. One set of analogue mode imagery was produced which presents the thermal data as varying densities on film which vary in direct proportion to the intensity of the recorded thermal signal. Analogue imagery is not quantified with respect to the black body reference sources. A second set of imagery in the 8-Level Sliced Mode was produced which presents the thermal data as six stepped gray shades on film, along with clear and black film to indicate thermal signal levels below and above the selected thermal signal range. 8-Level Sliced imagery are quantified with respect to black body reference sources.

4.0 METHODOLOGY

4.1 Fundamental Principles

All matter above absolute zero (00K) emits radiant energy in proportion to its temperature (Figure 1). As the temperature of an object increases the intensity of the radiant emissions increase and the peak of the radiant emission curve shifts towards the shorter wavelengths. In the electromagnetic spectrum, a temperature related progression exists from the thermal infrared to the near infrared, through the visible and into the ultra violet portion of the spectrum (Figure 2). Modern detectors of radiant emissions are selected according to the portion of the spectrum in which their detectivity is at an optimum level (Figure 3). The choice of a detector is partially determined by the temperature of the matter to be detected as it defines the portion of the spectrum in which radiant emissions will occur. The earth has a surface temperature of 300° K for most practical purposes. At that temperature, a black body radiant emitter has an emission curve that peaks at 9.7 micrometers. The detector chosen to image matter close to the ambient temperature of the earth should, therefore, be sensitive to the emissions at or near to 9.7 micrometers.

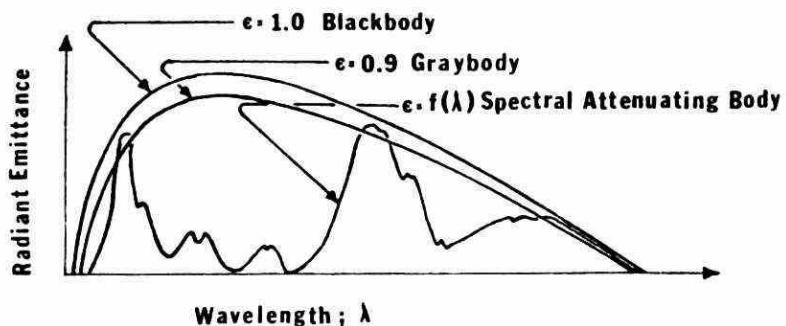


Figure 1 Spectral Distribution (For $\epsilon=1, 0.9$ & $f(\lambda)$)

To utilize airborne thermal sensors, atmospheric attenuation should be at a minimum. In the thermal infrared portion of the spectrum CO_2 , H_2O and O_3 are major attenuating agents, blocking radiant emissions at specific wavelengths. However, two large transmission windows exist between 8 to 14 micrometers in the long wave and 3 to 5 micrometers in the short wave portion of the thermal infrared spectrum (Figure 4).

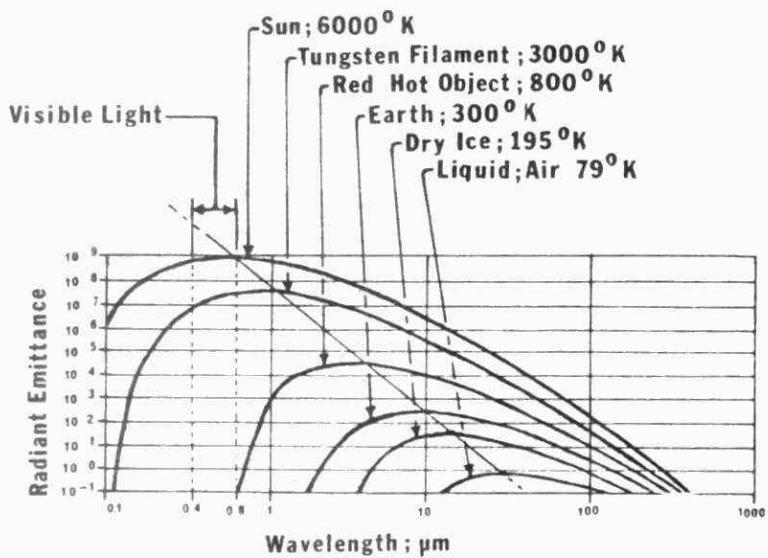


Figure 2 Spectral Blackbody Emittances

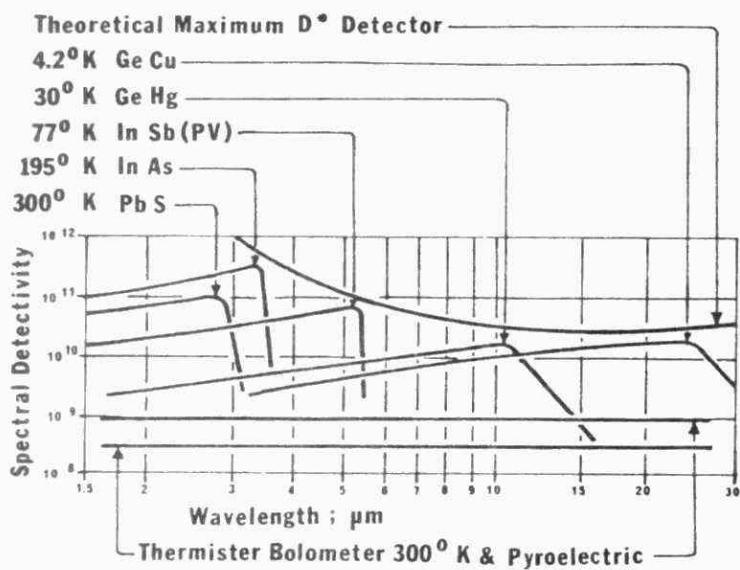


Figure 3 Long Wave Sensitivity & Detector Temperature

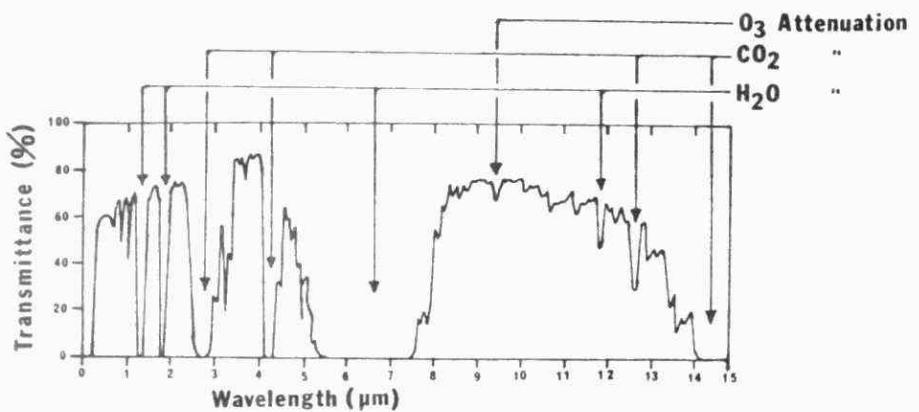


Figure 4 Atmospheric Transmission

4.2 Thermal Infrared Linscanners

An infrared linescanner uses a spot detector (HgCdTe at 780K) to generate a voltage proportional to the radiant emissions focussed onto the detector. This analogue voltage is amplified and stored on magnetic tape. A scanline is imaged by a rotating angular mirror which reflects into the optical elements of the scanner the radiant emissions from a line directly below the aircraft and perpendicular to the direction of flight (Figure 5). Electronic gating of the analogue voltages produced by the detector with reference to the rotation of the scan mirror defines the field of view of a scanner. The forward motion of the sensor platform ensures that the next scan line created acquires new data in the along track direction.

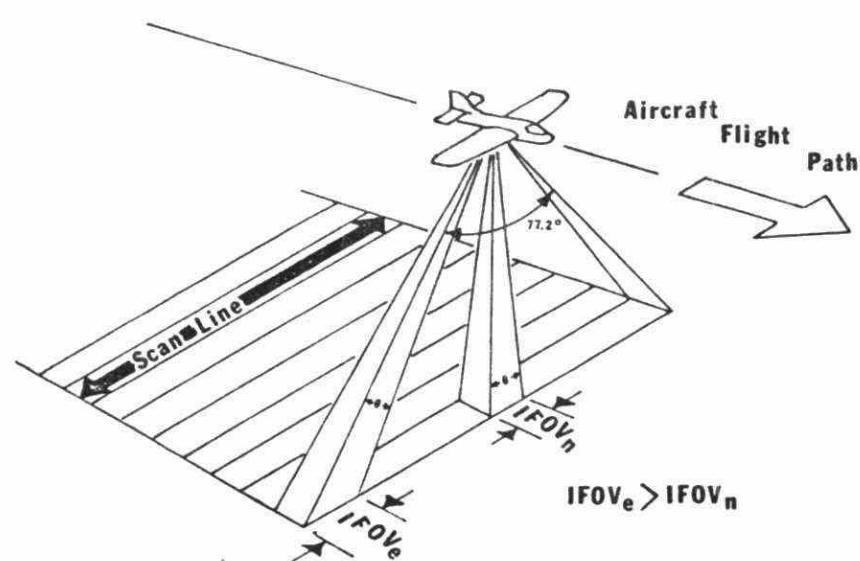


Figure 5 Infrared Line Scanning

In a quantitative scanner, black body reference sources are introduced on each side of the field of view. These reference sources are calibrated so that any desired temperature will be radiated by them and included in the recorded analogue signal. With one black body set below the minimum detected radiant emission from a scanned scene and the other black body set above the maximum, it is possible to assign equivalent black body radiant temperatures to the bracketed thermal scan by linear interpolation techniques (Figure 6).

Max. Interpolation Errors:

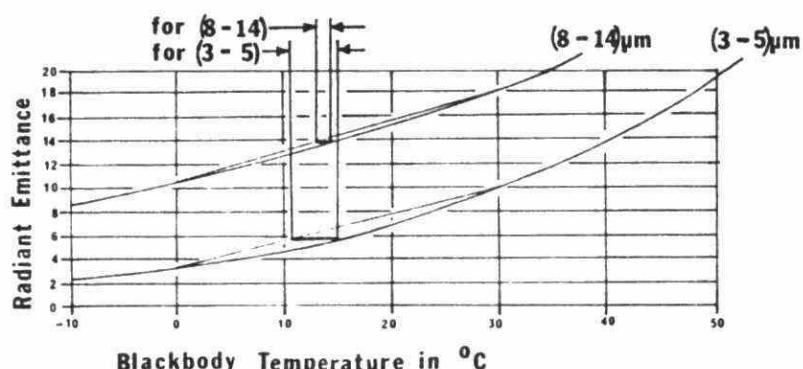


Figure 6 Linear Interpolation Errors

4.3 Imaging and Processing

To construct an image of the recorded thermal scene, the printer sweeps each individual scan line across a cathode ray tube. The intensity of the detected radiant emissions is proportional to the analogue voltages recorded on tape. These voltages determine the brightness of the cathode ray tube face. The sweep rate across the tube face is proportional to the acquisition scan rate (including S-bend correction). Film is transported across the CRT face perpendicular to the scan across the CRT and the film drive speed is determined by the acquisition V/H ratio, to reconstruct an accurate image of the sensed thermal scene.

For quantitative processing of data, the voltage values of the black bodies are sampled electronically and held for reference purposes. The voltage range defined by the black bodies is divided into six even divisions. Analogue voltages of each scan line are forced into whichever of the six divisions is closest to them in value (Figure 7). If the voltages fall outside the defined black body range, two other divisions indicating over and undershoots are available. The film exposed by this process shows clear to indicate radiant emissions below the low temperature black body; black for emissions above the high temperature black body; and six shades of gray for radiant emissions falling within the range of both black bodies. Since the calibrated temperatures of the black bodies are known, it is possible to assign equivalent black body radiant temperature ranges to each of the six gray shades.

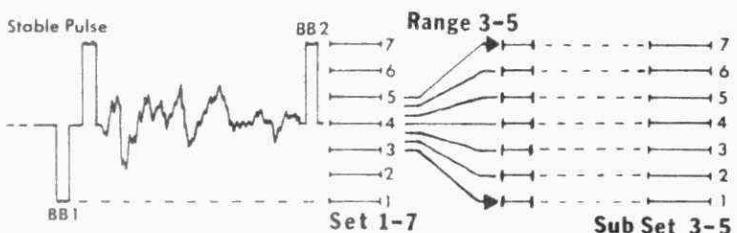


Figure 7 8-Level Slicing

4.4 Imagery

Flight lines were chosen to give the best synoptic view of the plumes on the particular date of the overflight. In total, seven sets of winter imagery were collected. Four flights were conducted over the Bruce Nuclear Power Development on Lake Huron (March 12, April 2, 16 and 17, 1980) and three flights over the Pickering Nuclear Generating Station on Lake Ontario (March 12, April 6 and 17, 1980). Due to editorial constraints, limited imagery are shown here and interested parties are invited to contact the MOE liaison officer for further details.

Figure 8 is a selected example of the near field thermal plume off the Bruce A N.G.S. This imagery was acquired on April 17, 1980 at an altitude of 1829 m (A.S.L.) at 10.47 hrs (EST). Data were processed in level slice mode with darker tones corresponding to cooler temperatures and lighter tones corresponding to warmer temperatures. Plant intake and discharge temperatures during the time of the flight were 2.4 and 11.1°C, respectively (Ontario Hydro operations data). The image frame is approximately 2.8 km x 3.5 km.

5.0 CONCLUSION

Airborne thermal infrared mapping systems offer an excellent cost effective method to acquire and display information on thermal plumes. Airborne thermal IR data provide:

- (1) information related to plume size, shape and orientation;
- (2) a synoptic overview; and,
- (3) a product that is easy to interpret.



Figure 8 Bruce A N.G.S. Thermal Plume April 17, 1980

THE PICKERING 'A' THERMAL PLUME
DURING THE WINTER MONTHS. SOME PRELIMINARY
RESULTS FROM A CO-OPERATIVE STUDY

R. R. Weiler
Lake Systems Unit
Water Resources Branch
Ministry of the Environment

November, 1980

- 1 -

1.0 Introduction

From December 1979 to the end of March 1980 the thermal plume from the Pickering Nuclear Generating Station A was studied by Ontario Hydro, National Water Research Institute and the Water Resources Branch, Ministry of the Environment. Staff from the Ontario Centre for Remote Sensing (Ministry of Natural Resources), the Regional Municipality of Durham, Metro Toronto and the Ministry of Labour provided additional support.

The objectives of the study were to characterize the behaviour of the thermal plume in winter by mapping its extent, shape and duration, under different meteorological and current conditions, and to characterize the dispersion characteristics of the nearshore zone.

The Pickering Nuclear Generating Station is located on the north shore of Lake Ontario, about 36 km east of Toronto (Figure 1.0 - 1). Its four CANDU heavy water generating units are rated at 540 MW each. The once-through cooling water (maximum $114 \text{ m}^3/\text{s}$, actual 90-100) is drawn from Lake Ontario through a 300-meter long channel between groins and is discharged through an open channel about 250 m west of the intake. The designed temperature rise through the cooling condensers is 11°C . A second similar nuclear station (Pickering B) is near completion immediately to the east of and adjacent to A. It will use the same intake channel, but the discharge will be on the east side of the site.

This paper, which describes some of the preliminary findings on the temperature regime near Pickering, is based on calculations and interpretation by the Ministry of the Environment of data collected and processed by Ontario Hydro, NWRI and the Ministry. A more complete analysis is expected in 1981.

2.0 Methods

2.1 Plume Surveys

On 8 occasions (January 29, February 5, 8, 12 and 20, March 4 and 20, April 1, 1980) Ontario Hydro measured temperature profiles in the plume using bathythermographs from boats (Ontario Hydro, 1980b).

The Ontario Centre for Remote Sensing (OCRS, 1980) flew infra-red radiometric surveys of the plume on 6 occasions (February 7, 12 and 28; March 6, 19 and 26, 1980). A PRT-5 infra-red sensor, which is sensitive to temperature changes of 0.1°C and has an absolute accuracy of $\pm 0.5^{\circ}\text{C}$, was used to measure the surface temperature.

2.2 Bottom Temperatures

Bottom thermographs were moored at sites shown on Figure 1.0 - 1. The instruments were located at the 5-meter contour east and west of Pickering A and on two transects east and west of the station. The thermographs used by Ontario Hydro have an overall accuracy of $\pm 0.2^{\circ}\text{C}$. The four thermographs supplied by MOE and moored furthest west have an overall accuracy of $\pm 0.6^{\circ}\text{C}$. A data base of hourly temperature readings from all the thermographs was established by Ontario and used in further analysis.

2.3 Currents

Fifteen current meters were moored at locations shown on Figure 1.0 - 1 by NWRI, Ontario Hydro and Ministry of the Environment. Two CATS platforms, fitted with bottom current meters and thermistor chains for temperature profiling, were installed at the Pickering and Ajax water intakes. All instruments, except three, gave almost continuous records for the whole period (NWRI, 1980).

3.0 Results

3.1 Meteorological Conditions

The winds blew chiefly from the northwest quadrant (58% of the time) with NW and NNW being the predominant directions (40%) and from the opposite quadrant for only 14% of the time. Resultant wind for the whole period was to 133° . The predominant speed range was between 10 and 20 km/h (50%). The distribution of wind directions and speeds does not differ markedly from those of previous years.

The winter was somewhat milder in December and January than average, with the average air temperature being 2.5°C and 1.5°C , respectively, above the 10-year means of -2.8°C and -6.1°C . In February, the average dropped to -7°C or 2° below the mean. Milder conditions returned in March and April when temperatures were slightly higher than average. As a result the onset of true winter conditions was somewhat delayed and less ice than usual was observed along the shore.

3.2 Currents

The two predominant current directions are 70° and 250° - that is, east and west along the shoreline. Examples of currents averaged over a month are shown in Figure 3.2 - 1. This basically bi-directional current pattern holds in a band from 1 km to 12 km from shore, with the frequency of eastward currents (to 70°) varying, at different moorings, between 33% and 58% and westward (to 250°) between 14 and 34%. The mean current speeds in this band averaged 10-23 cm/s to the east and 7-16 cm/s to the west. The frequency and speed of currents increased from the shore to about 3-5 km, after which they remained essentially constant. At moorings closer to the shore, its configuration has a greater effect. For example, at 79-00-21A the eastward currents occur only 15% and westward only 20% of the time, the average speeds are around 7 cm/s and the predominant current direction is towards the shore (NWRI, 1980). This pattern of bi-directional currents offshore was also observed at Pickering by Ontario Hydro in the winter of 1979 (60% to the east, 9% to the west).

The study period can be divided basically into alternating episodes of eastward and westward current, with a few episodes of currents in other directions. The change in direction occurred over a very short time, generally of the order of less than 12 hours. Fig. 3.2 - 2 shows 2 westward and 3 eastward current episodes and the effects on temperature as measured at bottom thermographs.

The first easterly period starts on December 28 and ends on January 2; the second starts on January 7 and ends on January 15; the third starts on January 18. The start of each episode is preceded by a period of slower currents (5 cm/s). The direction of the winds and the currents are roughly similar, although the second easterly episode is interrupted by periods of westerly winds. The direction of the winds is much more variable than that of the currents.

In general, eastward episodes are associated with warm temperatures as the plume impinges on the thermographs east of Pickering. The temperature does not decrease immediately after the current switches on January 2, but decays rather slowly to an average around 2°C, interrupted by periods of higher temperature. At the start of the third eastward period, there is a rather abrupt temperature increase and the plume front travels along the current until, by the time it reaches THB 27, it is no longer present. Although plume impingement on a particular location is closely linked to plume direction, it is also clear that residual temperature effects can occur and that effects of the plume can be observed even when, to judge by the currents, the plume is going in the opposite direction.

3.3 Plume Structure

Figure 3.3 - 1a, (Ontario Hydro 1980b) shows an extreme eastward plume (March 4) observed during the study. Other examples of plumes are shown on Figure 3.3 - 4a and 4b. Based on the 3°C isotherm as the edge of the surface plume, the length of the observed easterly plumes varied from about 4 to 11 km with the majority being around 5.5 km. The majority of westward plumes were less than 3 km long. The plumes were surprisingly narrow. In only two cases did the eastern plume exceed 2 km in width and the most common width was less than 1 km. The westerly plumes were somewhat wider.

The plume width at the bottom was somewhat greater than at the surface, though with long plumes the spreading is not large. Figure 3.3 - 1b gives the cross section of the March 4 plume at the A-A transect about 2.5 km from the outfall. The plume is close to being isothermal vertically and the lakeward edge has the characteristics of a front; that is, the temperature changes rapidly over a small distance. The near field structure can be much more complicated, as exemplified by a plume mapped on February 26, 1979 by Ontario Hydro (Figure 3.3 - 2a, b; Ontario Hydro 1979). Although a sharp front exists with the temperature dropping from more than 5°C to less 1°C at the surface over a few decameters, once the water has cooled below 4°C , the water spread along the bottom following the density gradients.

Between 1973 and 1979, Ontario Hydro (1980a) surveyed the Pickering NGS plume on 15 days and NWRI on 9 days between the months of December and April when the ambient lake temperature was less than 4°C . They observed eastshore plumes on 42% of those days (under W to NW winds), westshore plumes on 25% (winds from SE quadrant), offshore plumes on 17% (NNW to ENE winds), split plumes on 8% (SW winds), and plumes shifting from one shape to another on 8% of the survey days. Along their centre lines the cold weather plumes had temperatures above 4°C from surface to bottom. At plume leading edges, water had cooled to 4°C and below, sunk, and spread out along the bottom in the direction of plume movement underneath the ambient lake water. Along their sides, the cold weather plumes had steep horizontal temperature gradients and were almost isothermal vertically. Some sinking and spreading along the lake bottom was also observed at the sides of the plumes. Hydro's surveys did not go far enough from the outfall to define completely the extent of many of the cold weather plumes surveyed.

The only day when both Ontario Hydro and OCRS measured the plume was February 12, 1980. Although different in detail, the overall structures are the same (Figure 3.3 - 3a, b; Ontario Hydro 1980b, OCRS 1980).

3.4 Plume Impingement Along the Shore

The length of time the lake temperatures as measured by the bottom thermographs (5 m depth) are above the ambient can be used to trace the extent and frequency of occurrence of the plume. This method assumes that an ambient temperature can be selected and that there are no other major localized sources of heat besides the Pickering generating plant.

Ambient temperatures were derived by averaging the lake temperatures measured by thermographs which were not affected by the plume; that is, from either the three or four most easterly or westerly thermographs when the currents were to the west or to the east, respectively. Once the ambient was established, accurate to within $\pm 0.5^{\circ}\text{C}$, a four hour average temperature difference was used in computing the duration of temperature above ambient. A few examples of the duration-time curves are shown in Fig. 3.4-1.

The major river runoff period starts in the latter part of March and in early April. Indeed, the temperature patterns measured during the plume surveys of March 20 and April 1 show the effects of runoff at the mouths of Highland Creek and the Rouge River. Solar radiation will affect only a very thin surface layer and will affect the nearshore region uniformly. Further, as shown by the thermograph records for the east and west transects, the nearshore temperatures are significantly cooler than further offshore, a fact which may be attributed to the smaller depth and the proximity to the shore. The flow from the York-Durham sewage treatment plant outfall is around 10 MGD or $0.5 \text{ m}^3/\text{s}$, a very small fraction of the 90-100 m^3/s put out by Pickering. Therefore, it is unlikely that there are other major localized sources of heat besides the generating plant.

The percent of time temperatures were 0.5, 1, 2, 3, and 4 degrees Celsius above ambient were read from temperature-duration curves such as 3.4-1 and plotted as a function of distance from Pickering on Fig. 3.4-2a and 2b. A difference of 1.0 degrees is probably significantly different from the ambient.

It is clear from Fig. 3.4-2a and 2b that differences greater than two degrees can be observed as a significant percent to the time ($>25\%$) only close to the station; that is, closer than 5 km to the east and 1.5 km to the west. Temperature differences greater than this are confined to even smaller distances. Temperature rises of one degree are observed 5 to 10% of the time at the maximum distances - 17 to 20 km - where the thermographs were moored.

4.0 Summary and Conclusions

The currents in the period mid-December to end of March are basically parallel to the shore and predominately to the east (30 - 60% of the time) rather than the west (15 - 35%). Maximum speeds can reach 45 cm/s, although the average is around 15 - 20. The currents increase out to about 5 km and remain thereafter fairly uniform out to 12 km. Csanady (1970) has called such currents "coastal jets". Near shore, topographical features such as headlands will form localized subsidiary circulation patterns.

Because the currents are chiefly shore parallel and swift, the effects of the Pickering thermal effluent can be detected at considerable distances on both sides of the generating plant. Using 1°C as a significant rise above ambient lake temperatures, the effluent can be traced as far as 15-20 km east and west of the station 5 - 10% of the time in the winter. Temperature rises greater than 2°C can be observed a significant percent of the time ($>25\%$) only close to the station; that is, closer than 5 km to the east and 1.5 km to the west.

The Ministry of the Environment is continuing its analysis of the results of the thermal plume studies to determine their significance for water management in coastal areas.

Acknowledgement

The author wishes to thank R. Walker, R. Arden and R. Farooqui, from the Design and Development Division, Ontario Hydro, for processing data on temperatures, currents and winds measured by Ontario Hydro for this study. He also wishes to thank J. Bull and R. Murthy of the National Water Research Institute, Canada Centre for Inland Waters, for processing data on currents and temperatures measured by NWRI.

References

Csanady, G. T. 1970. Dispersal of effluents in the Great Lakes. *Water Res.* 4: 79-114 (1970).

Ontario Centre for Remote Sensing (OCRS), Ministry of Natural Resources, 1980. Infra-red radiometric survey over the Pickering Nuclear Generating Station. 17 p. and appendices.

Ontario Hydro, Design and Development Division. 1979. Lake Ontario Pickering NGS 'A': Thermal plume investigations - cold weather plume surveys February 1979. Report No. 79440. 3 p. and diagrams.

----- 1980a. Lake Ontario. Pickering Generating Station: Analysis of thermal plume surveys conducted 1971 to 1979. Report No. 80072. 31 p. and appendices.

----- 1980b. Lake Ontario. Pickering Nuclear Generating Station: Winter thermal plume study 1979-1980. Thermal plume mapping. Report No. 80294. 9 p. and diagrams.

National Water Research Institute, 1980. Coastal current climatology summary, Pickering Generating Station Dec. 6, 1979 to Mar. 31, 1980. 12 p and appendices.

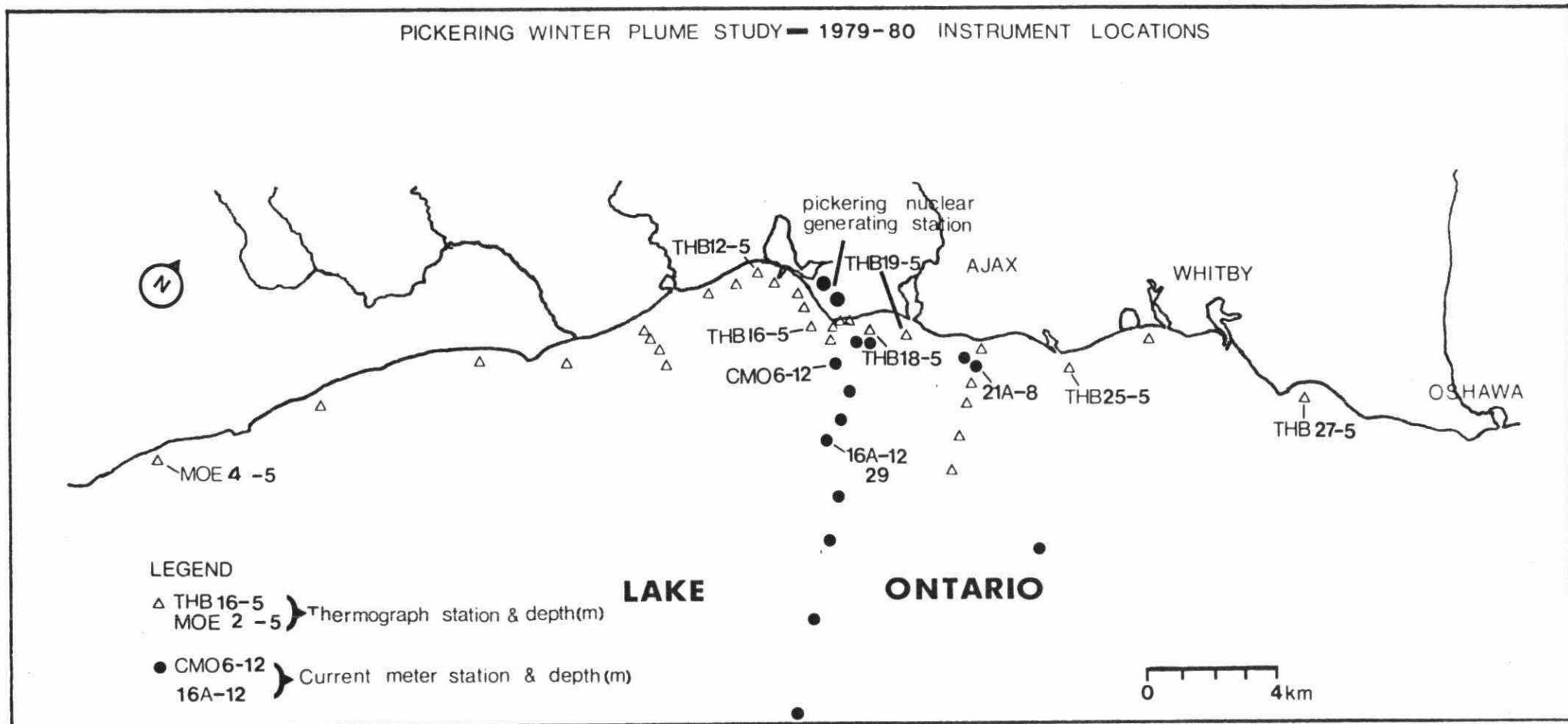
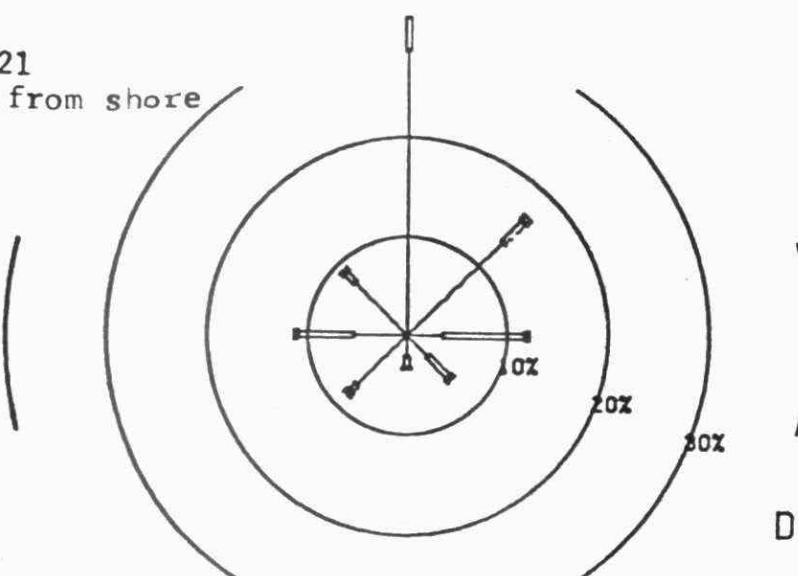


Figure 1.0-1

MOORING: 16, 21 DATE: FEB 1980
MONTHLY SUMMARY: CURRENT*

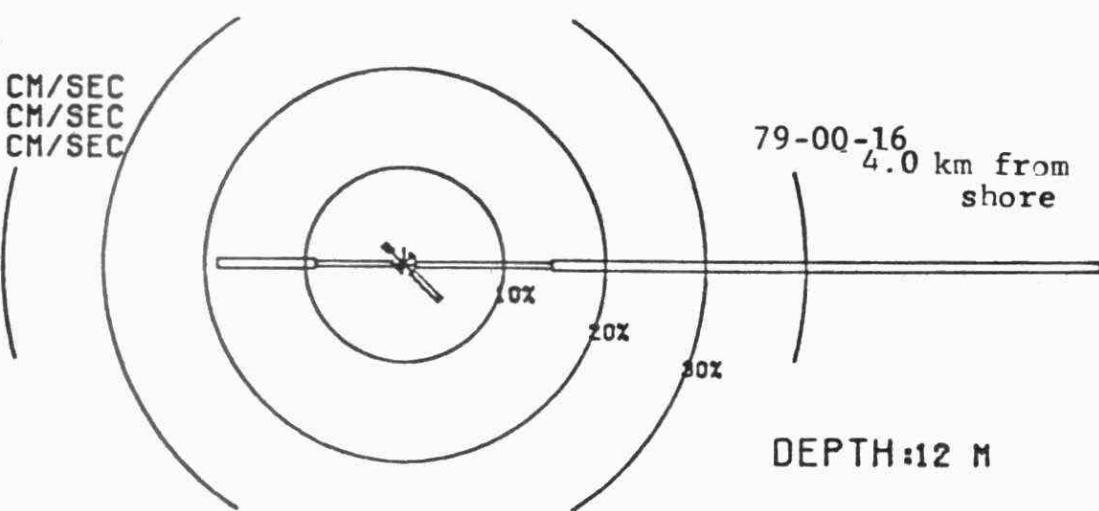
254

79-00-21
0.75km from shore



DEPTH: 8 M

CURRENT
— 0-5 CM/SEC
— 5-15 CM/SEC
— ≥ 15 CM/SEC



DEPTH: 12 M

* DIRECTION TOWARDS

FIGURE 3.2-1.

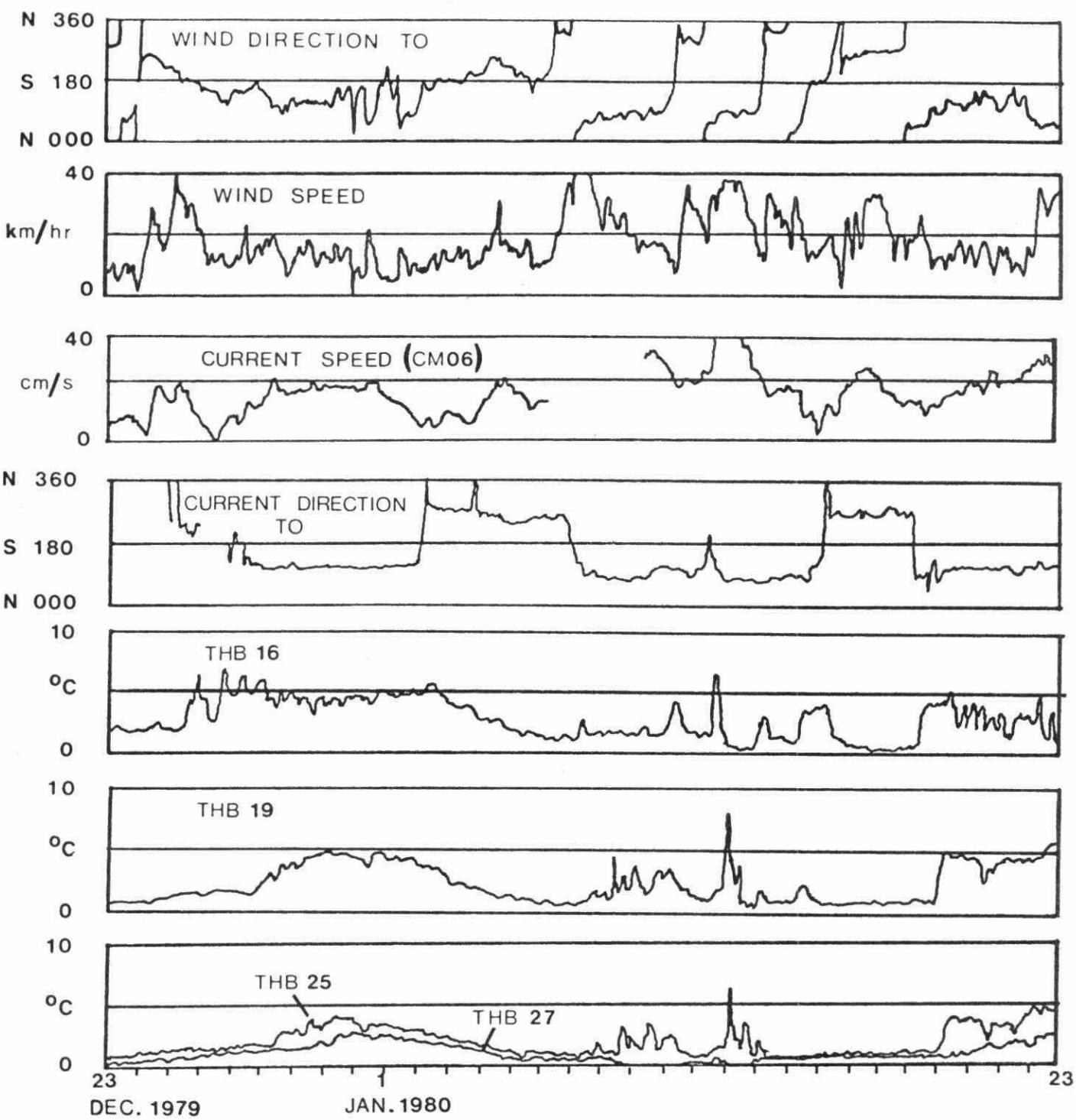


FIGURE 3.2-2. Wind direction and speed at Pickering 'A'; current speed and direction at mooring CM06 (12m depth); temperature at bottom thermographs THB 16 (1.2 km E of pickering 'A'), 19 (4.7 km), 25 (9.7 km) and 27 (17.2 km), all at 5m depth, for the period Dec. 23, 1979 to Jan. 23, 1980.

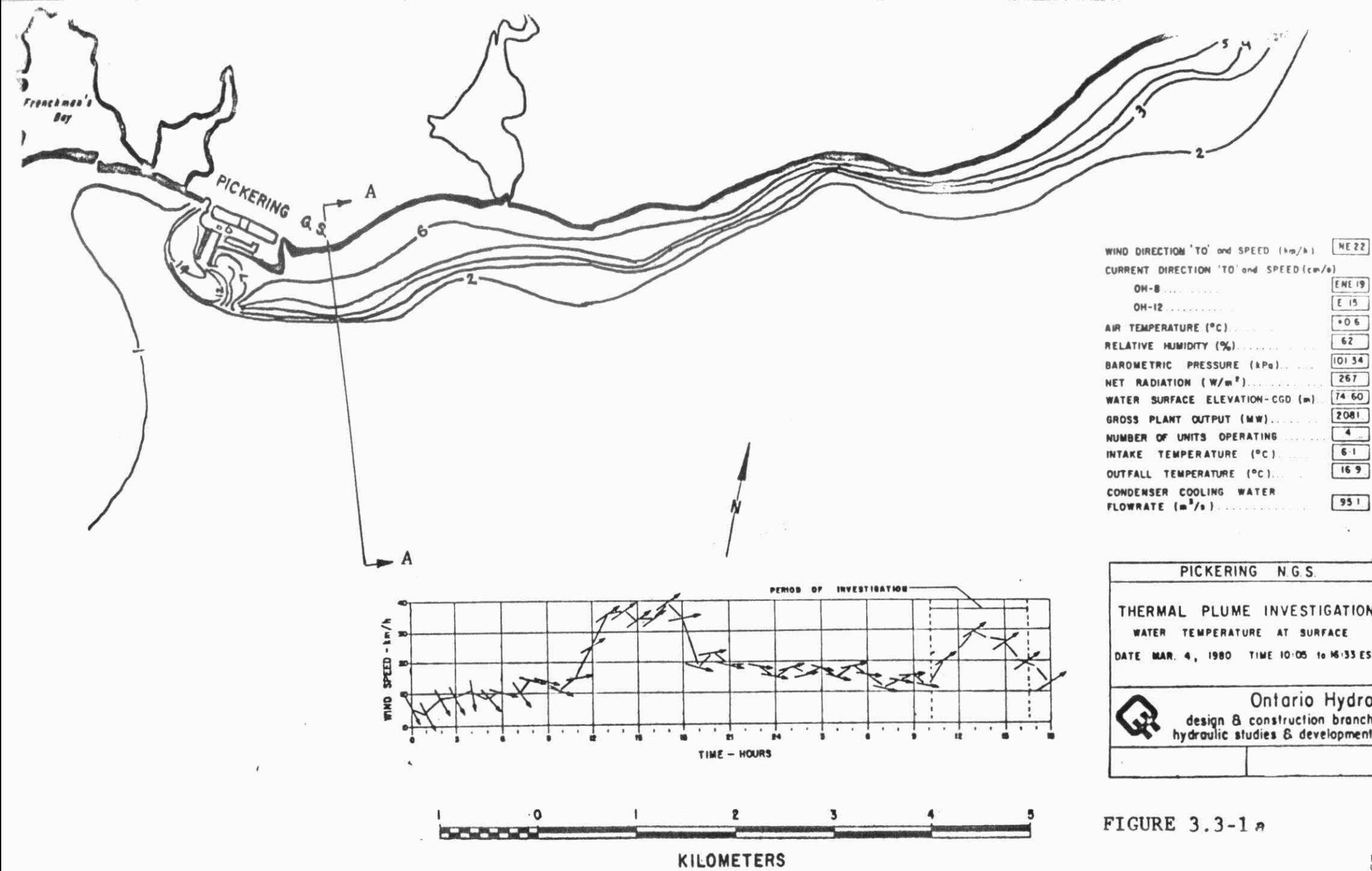
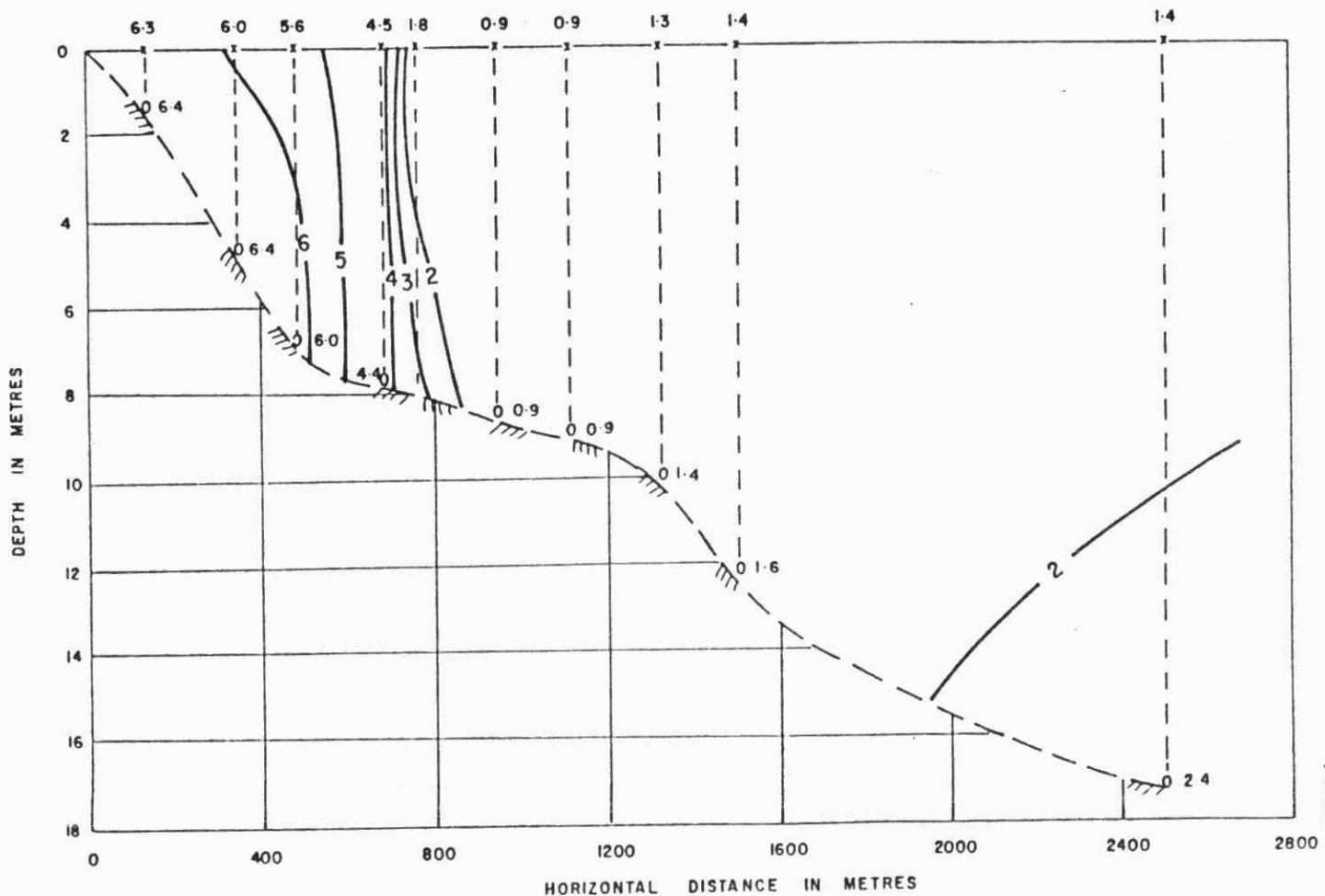


FIGURE 3.3-1a

PROFILE No	19	20	21	22	23	24	25	26	27	28
TIME (EST)	1112	1116	1119	1125 1127	1130	1133	1136	1139	1148	



LEGEND

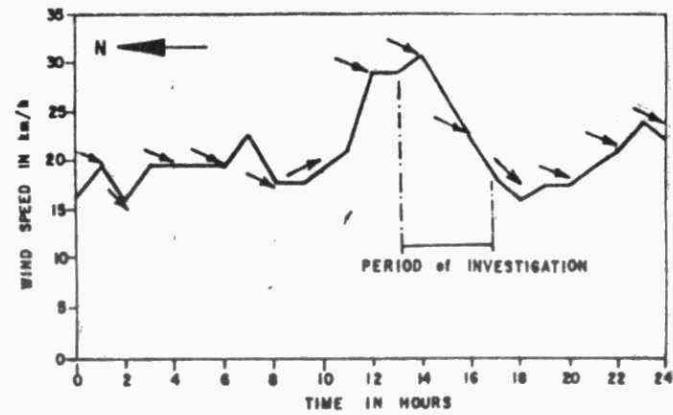
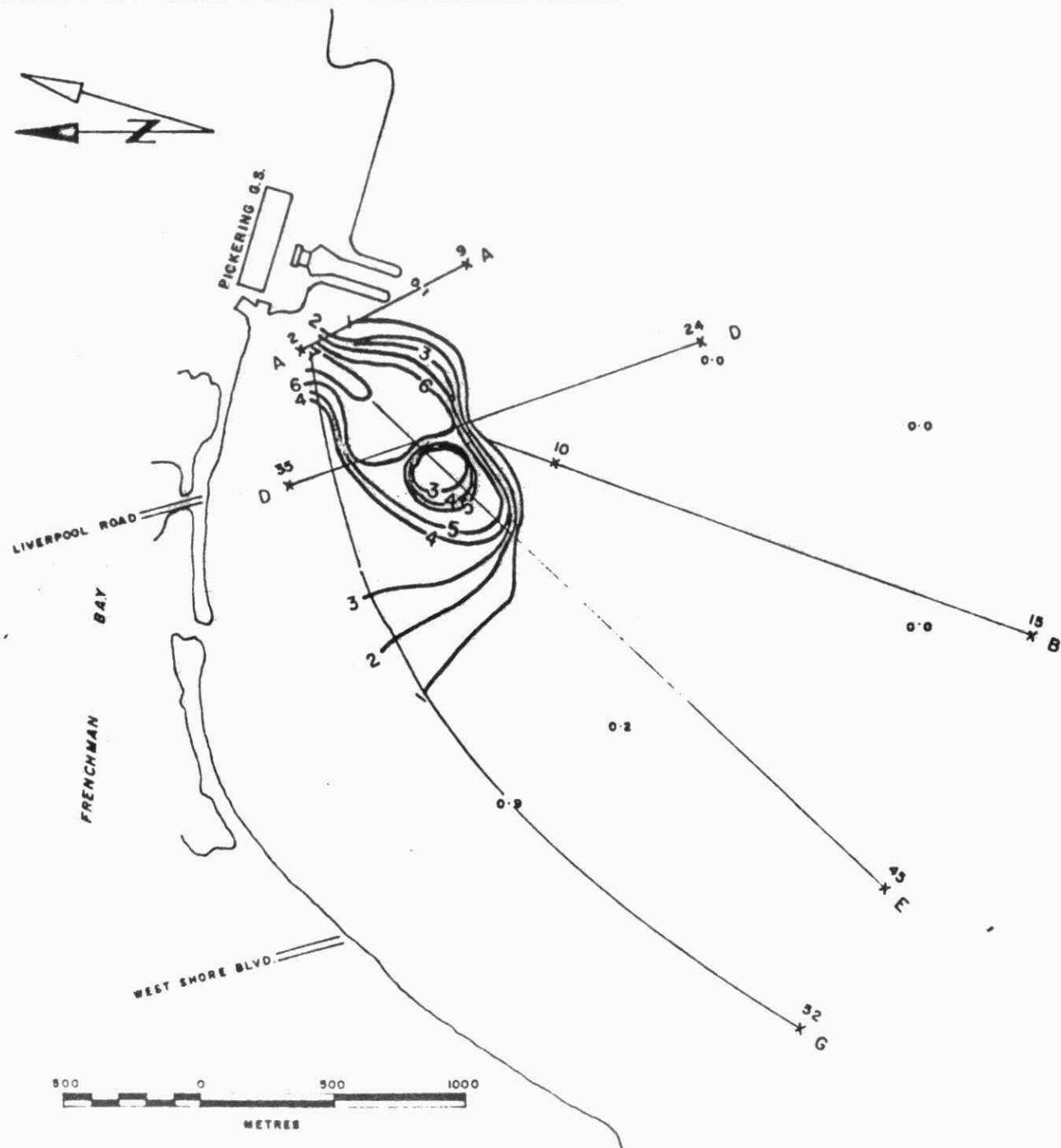
x SURFACE TEMPERATURE °C

o BOTTOM TEMPERATURE °C

PICKERING N.G.S.
THERMAL
PLUME INVESTIGATION
WATER TEMPERATURES AT SECTION A-A
DATE MAR. 4, 1980 TIME 11:12 to 11:48 EST

Ontario Hydro
design & construction branch
hydraulic studies & development

FIGURE 3.3-1b



WIND

LEGEND

SECTION LOCATION → KEY PROFILE POSITION & NUMBER ← 99

PICKERING "A" G.S.

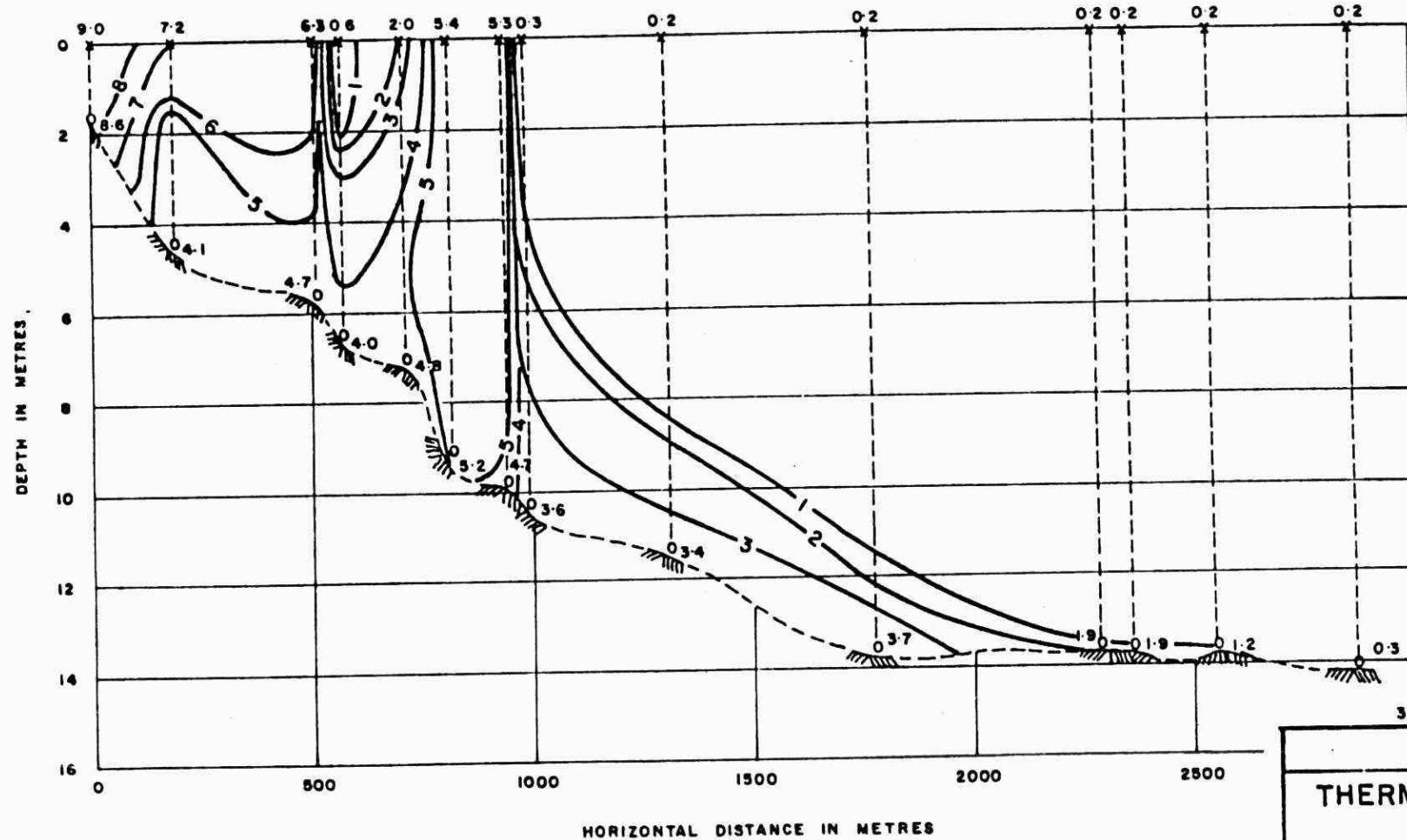
THERMAL PLUME INVESTIGATION
SURFACE WATER TEMPERATURE
26 FEB. 79 TIME-1323 to 1651 EST



design & construction branch
hydraulic studies & development

FIG. 3.3-2a

PROFILE No	60	36	32 37	38	39	41 40	42	43	44 47	46	48
TIME (EST)	1651	1644	1517 1519	1524	1527	1530	1534	1547	1544	1540	



LEGEND

X / SURFACE TEMPERATURE °C
O / BOTTOM TEMPERATURE °C

PICKERING 'A' G.S.

THERMAL PLUME INVESTIGATION
SECTION E
WATER TEMPERATURE
26 FEBRUARY, 1979

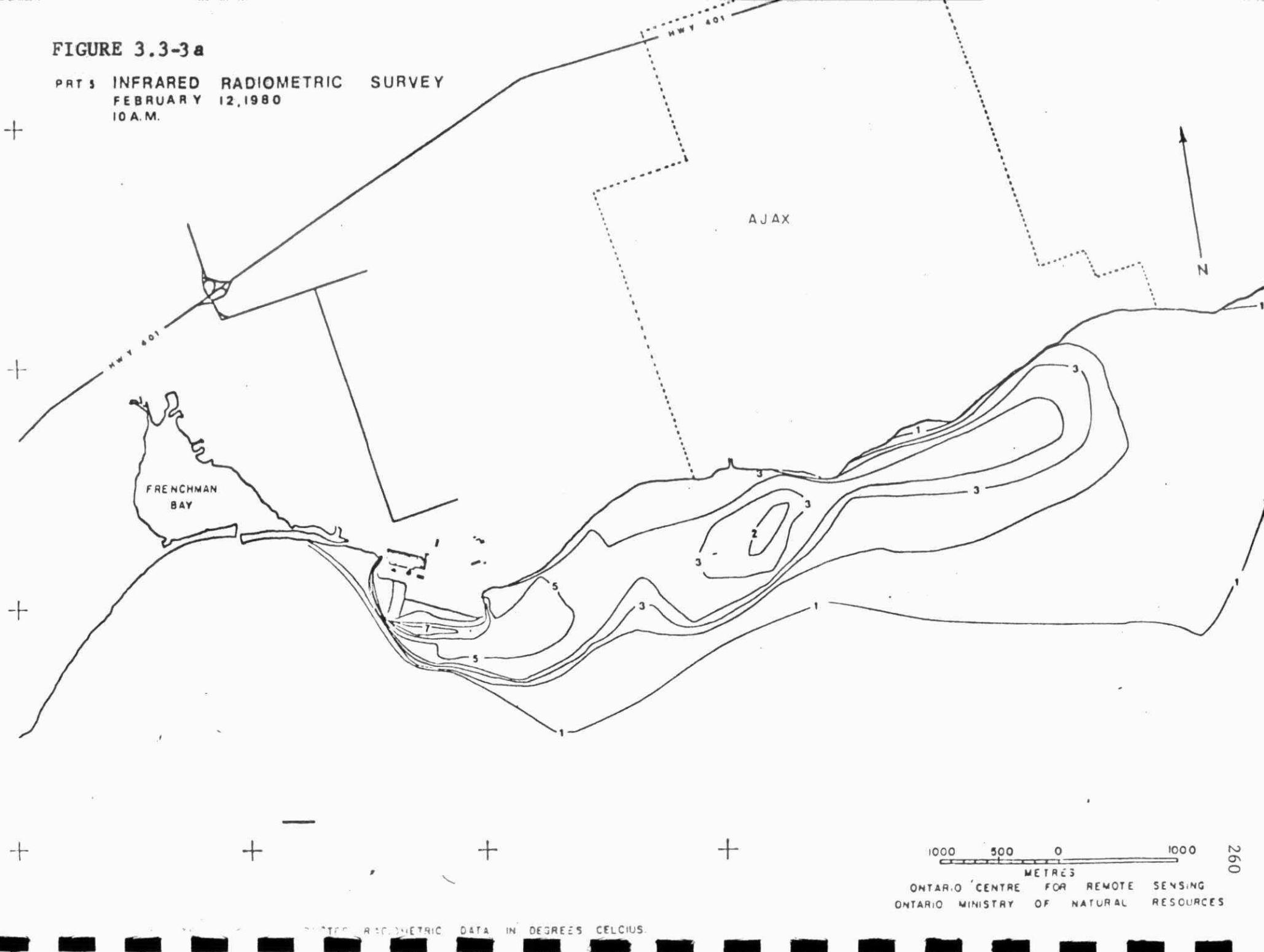


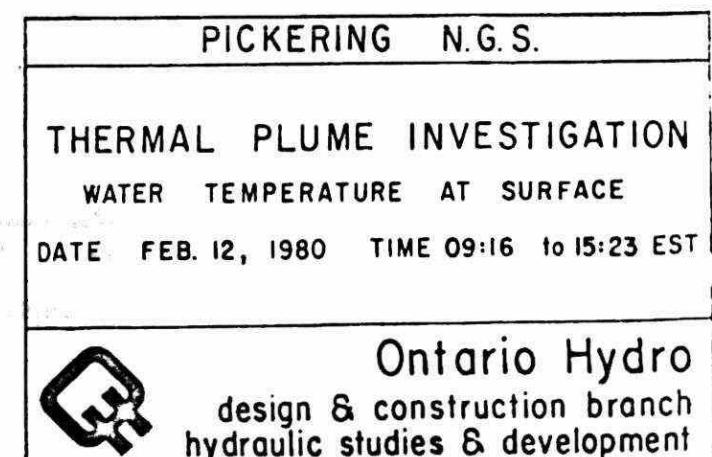
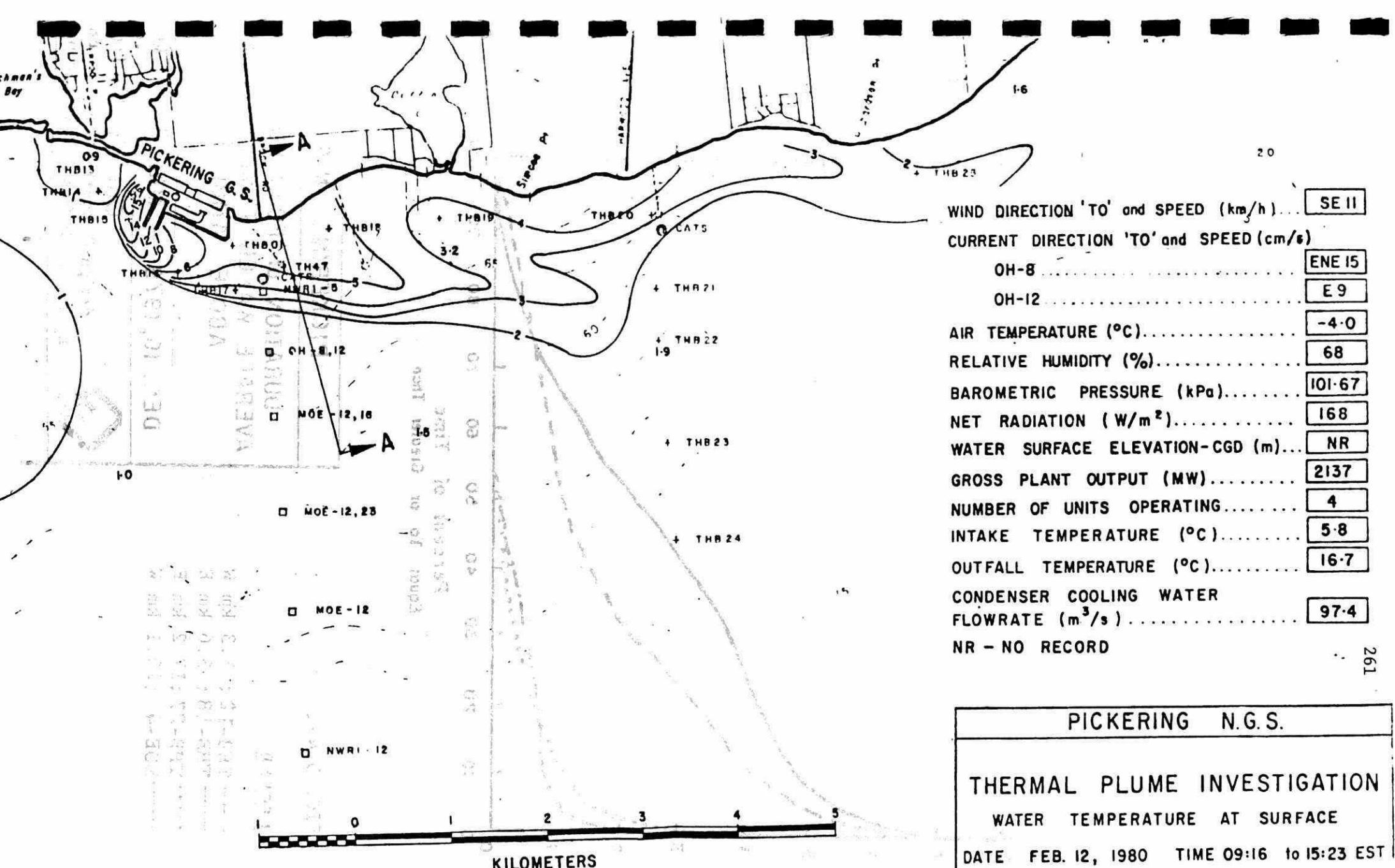
Ontario Hydro
design & construction branch
hydraulic studies & development

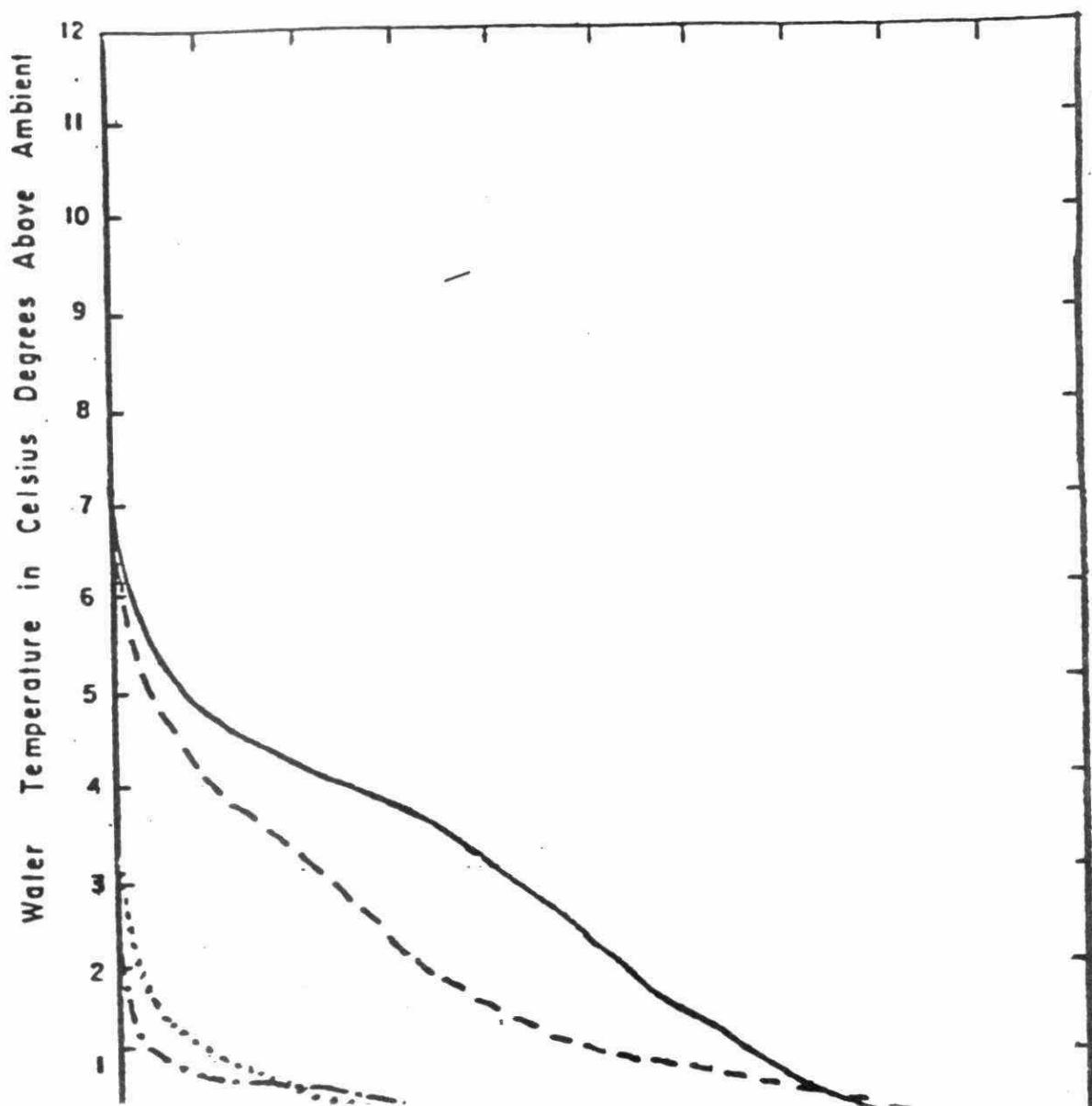
FIG.3.3-2b

FIGURE 3.3-3a

PRT 5 INFRARED RADIOMETRIC SURVEY
FEBRUARY 12, 1980
10 A.M.







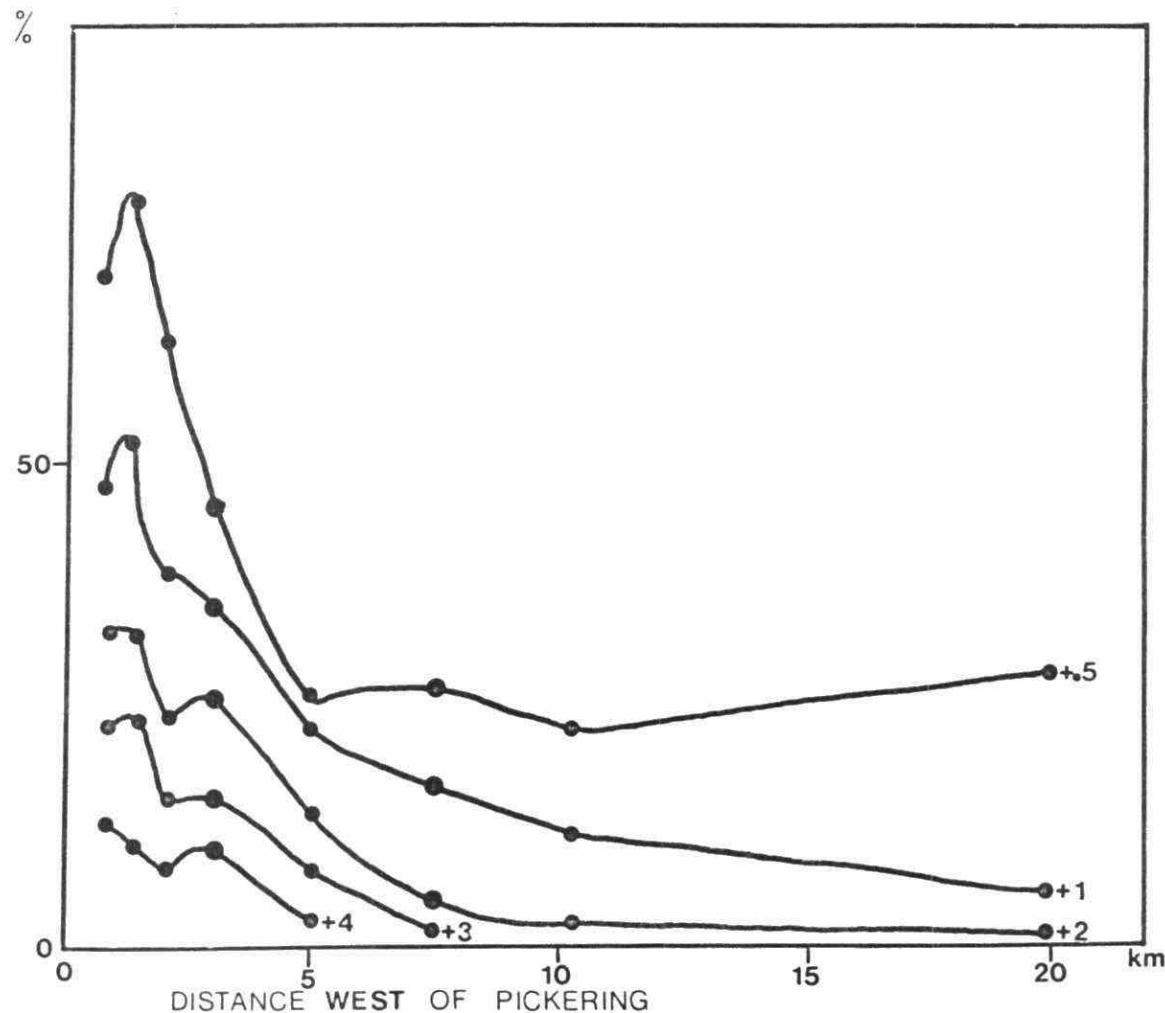
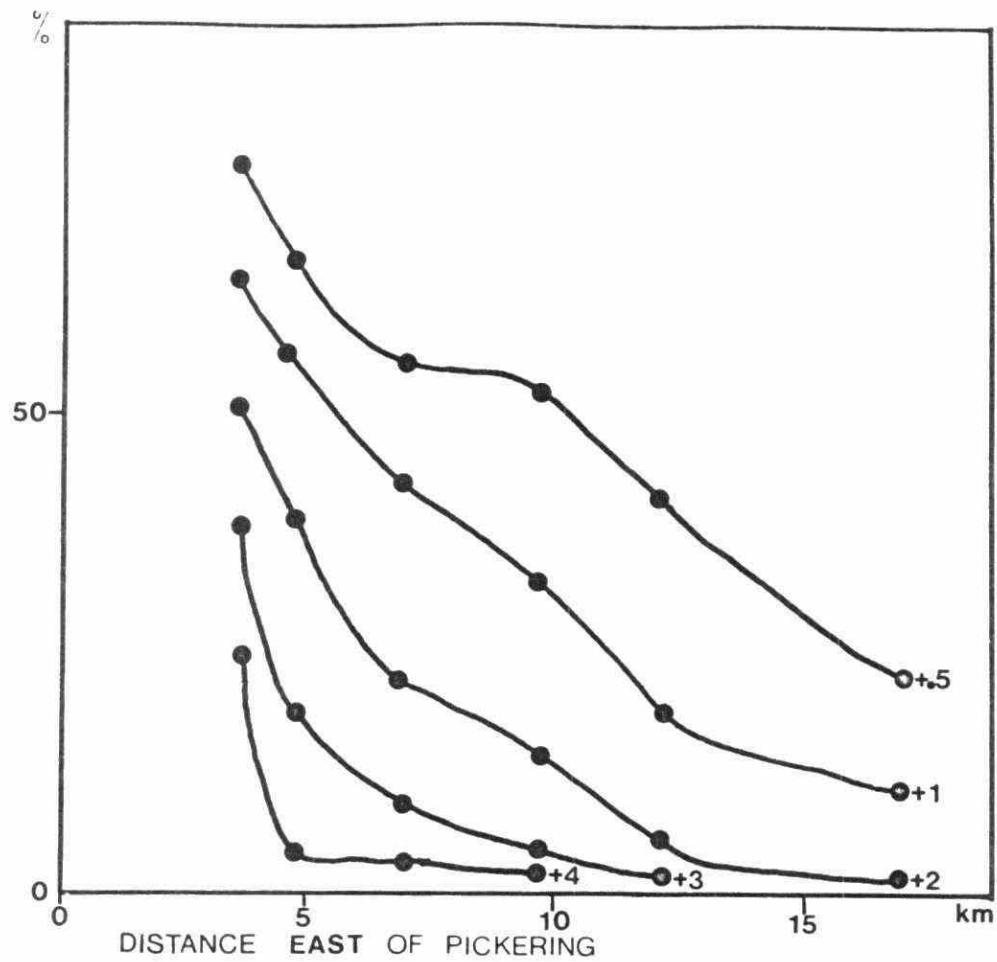


Figure 3.4-2 .

Duration of Temperature rise $\Delta T = T - T_{\text{ambient}}$ ($^{\circ}\text{C}$)

as a function of distance from Pickering for $+0.5 \leq \Delta T \leq 4.0$

The Uptake of Methylmercury²⁰³ by
Walleye (Stizostedion vitreum vitreum)
through a Simulated Ecosystem as a
Function of Selected pH Regimes

Watson, T.A.¹, J.S. Langan and T.J. Wheaton

MacLaren Engineers Planners & Scientists Inc.
Suite 100
1220 Sheppard Avenue East
Willowdale, Ontario
M2K 2T8

¹ Present Address: Department of Biological Sciences
Simon Fraser University
Burnaby, British Columbia
V5A 1S6

ABSTRACT

The uptake of methylmercury²⁰³ in walleye (Stizostedion vitreum vitreum) and rainbow trout (Salmo gairdneri) from water and diet was investigated over a period of five days at pH 5.0, 6.0 and 7.0 in four stainless steel columns (1 m x 4.5 m) of 3500 L capacity.

Relative accumulations of methylmercury²⁰³ by walleye and trout were monitored in fish that were: (1)-starved; (2)-fed methylmercury²⁰³ labelled food; and (3)-fed unlabelled food. Rainbow trout were tagged with methylmercury²⁰³ which was added to their water and zooplankton forage base (Daphnia magna). Methylmercury²⁰³ was added to the columns or ecosystem simulators as methylmercuric²⁰³ chloride to yield a final approximate concentration of 4 ng/L in the vessels.

Daphnia (D. magna) acquired greater amounts of methylmercury²⁰³ at pH 7.0 compared with those at pH 6.0. Rainbow trout also accumulated the most methylmercury²⁰³ at pH 7.0 and uptake was linear during a five day exposure. Methylmercury²⁰³ accumulation was the highest in trout fed labelled Daphnia while those deprived of Daphnia accumulated roughly one-third the quantity of feeding trout. The relative contributions of methylmercury²⁰³ to trout from water and food was of the same magnitude.

Uptake of methylmercury²⁰³ by walleye from trout was not affected by pH. Walleye fed methylmercury²⁰³ tagged trout accumulated twice as much of the isotope compared with fish that were starved or fed with unlabelled trout. Less than 15% of the amount of methylmercury²⁰³ in trout fed to walleye was retained while the remaining 85% was presumed to have been eliminated. Acidity did not affect the retention or elimination of methylmercury²⁰³.

Results of this study suggest that methylmercury uptake by fish in acid-stressed waters may not be greater than for those in pH neutral areas. This observation may be related to a slower elimination rate of the compound by aquatic organisms in pH neutral environments.

ACKNOWLEDGEMENTS

Appreciation is extended to Dr. A. Niimi and Messrs. K. Suns, G. Craig, C. Innis and D. Rodgers for their support and criticisms. We would also like to express our gratitude to the White Lake Hatchery of the Ontario Ministry of Natural Resources for supplying the walleye used in this study. The assistance of Mr. Dave Troubridge is appreciated for conducting bioassays of Daphnia magna tolerance to acidity.

INTRODUCTION

The effects of mercury contamination and acid precipitation on the aquatic environment are currently receiving a great deal of attention. Mercury is perhaps the most ubiquitous of the toxic heavy metals in the aquatic environment, but it is generally found at low (ng/g or $\mu\text{g/L}$) concentrations (Huckabee *et al.*, 1975). The causes of acid precipitation have their roots in the present and historical uses of fossil fuels, especially coal, for energy. Acid precipitation is formed in the atmosphere where emitted compounds of sulphur, chlorine and nitrogen are converted to sulphuric, hydrochloric as well as nitrous and nitric acids (Likens *et al.*, 1979).

The movement of mercury in the aquatic environment is significantly affected by its methylation in sediments followed by methylmercury's entry into every trophic level of the aquatic ecosystem (Jernelov and Lann, 1971). Methylmercury is concentrated in aquatic organisms by direct uptake from water and diet, with the latter route apparently being the most important (Norstrom *et al.*, 1976; Phillips and Russo, 1978; Phillips and Buhler, 1978). There is a tendency for predator fish and organisms at higher trophic levels to contain the greatest amounts of methylmercury (Jernelov and Lann, 1971; Krenkel, 1974).

Acid precipitation has caused great economic and aesthetic losses in the aquatic environment due to the extirpation and reduction of fish populations. Increased acidity causes a general decline or reduction in numbers of fish species with some of the more desirable species being affected over a pH range as high as 5.5 to 6.0 while others show tolerance to a range as low as 4.5 to 4.7 (Harvey, personal communication). Primary productivity does not appear to be affected by acidity, although a simplification of phytoplankton communities has been reported (Kwiatkowski and Roff, 1976). The tolerance of zooplankton to increased acidity appears to be quite limited as *Daphnia pulex* do not reproduce below pH 7.0 (Davis and Ozburn, 1969). Sprules (1975) found that many species do not occur below pH 5.0 in acid stressed lakes, similar observations have been reported by others (Carter, 1971; Salazkin, 1971; Harvey, 1975; Roff and Kwiatkowski, 1977).

Acid precipitation has been known to kill fish in field situations. Fish kills have been reported after periods of heavy rain and spring snowmelt due to the acid pulse in receiving waters (Leivestad and Muniz, 1976; Leivestad *et al.*, 1976). The prolonged impacts of acid precipitation and declining pH seem, however, to have their greatest effects on fish recruitment. Recruitment failure may occur as a result of acid-induced mortality of fish eggs and/or larvae (Schofield, 1976). Mortalities in early life stages can alter the average age of fish populations and shift the size and age structure to larger and older fish (Ryan and Harvey, 1979). The direct effects of acid-induced mortalities to eggs and larvae have been demonstrated in a number of laboratory studies (Johansson *et al.*, 1973; Mount, 1973; Menendez, 1976; Craig and Baksi, 1977).

The impacts of acid rain have attained a new significance with the observation that the toxicities of various metals such as aluminum, zinc, cadmium, lead, arsenic, copper and mercury are increased as a result of declining pH (Schindler, 1979; Suns, personal communication).

Schindler has stated, in fact, that concentrations of certain metals have been reported in Scandinavian lakes at levels which are within two to three times the values that have been shown to have toxic effects on fish.

The increasing tendency for acidification of receiving waters by acid precipitation may have implications on the uptake and bioaccumulation of methylmercury through the aquatic food web. Increased acidity affects the partitioning of methylmercury between water and sediments. Miller and Akagi (1979) found, for example, that the amount of methylmercury in the water increased as pH decreased. This decrease in pH did not, however, affect the total amount of methylmercury generated in the sediments. Miller and Akagi (1979) suggested that these observations could quantitatively explain the elevations in mercury levels of fish taken from lakes of low pH. Suns *et al.* (1980) have also observed that fish in acid-stressed lakes exhibit higher concentrations of the metal due to depressed pH. The effect of pH on mercury uptake has also been investigated in the laboratory. Tsai *et al.* (1975) exposed fathead minnows (Pimphales promelas) and emerald shiners (Notropis atherinoides) to various concentrations of mercuric chloride in water and found that mercury uptake increased as pH decreased, with uptake increasing sharply at pH values below 7.0.

It is apparent that our understanding of mercury movements and accumulations through aquatic ecosystems has increased in recent years. With the addition of acid inputs, however, we are now faced with a completely different dimension of mercury transport in aquatic environments, one which we do not fully comprehend. It is obvious that research must be undertaken to characterize the movements of the metal's various forms through aquatic organisms as a function of depressed pH. The most important chemical form in this respect is the methylated species in view of its high affinity for biological tissues (Phillips and Russo, 1978).

This study was designed to investigate some aspects of methylmercury transport and accumulation through an aquatic food chain as a function of depressed pH. In this study methylmercuric²⁰³ chloride has been added to an aquatic ecosystem which has been simulated in large (1 m x 4.5 m) stainless steel columns of 3500 L capacity. The research was carried out at the Great Lakes Biological Laboratories at Burlington, Ontario. Water samples used in the experiments were collected from selected lakes in the Muskoka region of Ontario. These lakes demonstrated physical and chemical parameters typical of lakes that are subject to the effects of acid precipitation. A representative array of organisms was chosen for specific trophic levels in the simulated ecosystems and included: primary producers (indigenous algae); zooplankton or primary consumers (Daphnia magna); a secondary consumer, rainbow trout (Salmo gairdneri); and a top predator or tertiary consumer, walleye (Stizostedion vitreum vitreum). The uptake of methylmercury²⁰³ from water by these organisms was evaluated.

MATERIALS AND METHODS

Selection of Study Lakes

All of the lakes considered as potential candidates were within the Muskoka-Haliburton region of Southern Ontario. The main criteria for selection of study lakes was their susceptibility to the effects of acid precipitation and accessibility. Lakes affected by acid precipitation are typified by poor buffering capacity and characteristically display low hardness and alkalinity levels. Lakes within the Muskoka-Haliburton region exhibit relatively low pH and have depressed alkalinites ranging from 14 to 200 $\mu\text{g/L}$ (Dillon *et al.*, 1977).

Selection of the lakes was initially accomplished by studying topographical sheets to locate lakes of similar size and geographical placement. Data collected in previous years on pH, alkalinity, location, climatic factors and morphometry for selected lakes were also considered in the selection process.

Based on the above criteria, a list of 15 potential lakes was derived and each lake was visited in January 1979 to obtain data on accessibility, physiochemical properties and topography. Water samples were taken through the ice at a depth of 0.5 m with a Kemmerer sampler. Samples were analyzed for heavy metal content (cadmium, copper, lead, zinc and mercury) and total dissolved solids. Analyses were performed by atomic absorption spectrophotometry. Measurements of pH, alkalinity and hardness were also determined. Acidity was measured with a portable pH meter (Fisher Accumet, Model No. 150) and hardness and alkalinity were estimated according to Rand *et al.* (1976).

Collection and Maintenance of Experimental Organisms

Phytoplankton, indigenous to the study lakes were used in this study. However, pure stock cultures of the phytoplankton, Chlorella vulgaris were used to maintain Daphnia magna prior to placement in the ecosystem columns. The Daphnia were obtained from the Great Lakes Biolimnology Laboratories (GLBL) at Burlington, Ontario and were maintained in dechlorinated Lake Ontario water at 18-25°C.

Rainbow trout (mean weight ≤ 1 g) were purchased from Goosen's Trout Farm, Otterville, Ontario. The trout were maintained in dechlorinated Lake Ontario water at 15-18°C and compressed air delivered a supply of oxygen to the holding tanks. Two trout from this population were sacrificed for mercury analysis to monitor background concentrations prior to use of the stock in the uptake experiments. The fish were fed ad libitum on a commercially prepared diet (Martin Feed Mill Co., Elmira, Ontario).

Walleye (mean weight ≈ 12 g) were donated by the White Lake Hatchery of the Ontario Ministry of Natural Resources (Perth, Ontario) and were maintained under conditions similar to those described for the rainbow trout. The walleye would not accept pellet food, consequently they were fed ad libitum with either young rainbow trout or a locally purchased baitfish (Notemigonus crysoleucus). One walleye was sacrificed to monitor the background concentration of mercury prior to use of these fish in the experiments.

Acid Toxicity to Daphnia

The pH sensitivity of Daphnia was investigated in acutely lethal bioassays prior to use in the ecosystem simulators. Daphnia which were: (a) fed Chlorella and (b) deprived of the phytoplankton were exposed to a pH range from 5.0 to 7.0 at 18°C in 250 mL Erlenmeyer flasks. The bioassay procedures roughly followed those described by Sprague (1973). Mortalities were monitored over 192 hours and were expressed as a cumulative percentage.

Lake Column Simulators

Lake column simulators are stainless steel, cylindrical, high volume, indoor enclosures, that simulate open-water conditions in a lake. The columns used at GLBL are 4.5 m high, 100 cm in diameter and have a volume of 3500 L. Light is supplied by a 1000 W tungsten-halogen lamp on a 12 h photoperiod. Further details of the simulators have been described by Hodson and Millard (1977).

Isotope

Methylmercury as methylmercuric²⁰³ chloride ($\text{CH}_3^{203}\text{HgCl}_2$) was obtained in two separate shipments from New England Nuclear, Boston, Massachusetts.

Isotope shipments were diluted with distilled water to specific activities approximating 10 $\mu\text{Ci}/\text{mL}$ and stored under refrigeration in rubber-stoppered Wheaton glass serum bottles wrapped in aluminum foil.

The relative amounts of organic to inorganic mercury in both shipments were determined by phase separation (Rodgers, personal communication). Standard reference solutions of known methylmercury²⁰³ concentration were prepared for each shipment. These standards were monitored for radioactive decay on a regular basis and a decay curve was calculated for each set. These standards were used to estimate methylmercury²⁰³ levels in water and animals during the experiment. Estimates of radioactive methylmercury are given throughout the text as methylmercury²⁰³ and not as the chloride salt of the compound.

Experimental Protocol

Nine methylmercury²⁰³ uptake experiments were conducted using lake water samples from Atkins, Wood and Walker Lakes.

Samples of lake water (3000 L) were collected using chemically inert and clean equipment provided by the Ministry of the Environment (MOE). Lake water was subsequently transported by tanker to GLBL, generally within 12 hours. Water volumes in the columns were made up to 3500 L by the addition of deionized water prepared to simulate the water quality indigenous to the study lake.

Five days prior to addition of methylmercury²⁰³, walleye (12-30 g) and rainbow trout (1.0-1.5 g) were caged and placed in the columns for acclimation to experimental conditions. Cages were fabricated from 6.8 litre plastic pails with ports covered by fibreglass screening of adequate diameter to preclude access by Daphnia magna, yet sufficient to permit water cycling. Feeding was facilitated through an aperture with

a removable cover. Cages were weighted and suspended in the columns at depths ranging from 1 to 4 m.

Nine walleye were introduced to each column. Experimental feeding conditions were as follows:

- (a) Three walleye were individually caged and fed during the experiment with rainbow trout previously exposed to methylmercury²⁰³ through their diet and column water. The trout were weighed and counted for methylmercury²⁰³ activity prior to presentation to walleye. This group of walleye was referred to as "Hot fed";
- (b) Another group of three walleye was placed in a single cage and fed during the experiment with rainbow trout which had not been exposed to methylmercury²⁰³. This group was referred to as "Cold fed";
- (c) A final group of three walleye was placed in a single cage and starved during the experimental period. This group was referred to as "Starved".

Rainbow trout were placed only in the pH 6.0 and pH 7.0 columns as they would not survive the pH 5.0 regime. Feeding conditions of the "hot fed" walleye at pH 5.0 were, therefore, satisfied with rainbow trout which had been exposed to methylmercury²⁰³ in the pH 6.0 treatment columns.

Each pH 6.0 treatment column received 18 rainbow trout while each pH 7.0 treatment column received 9. Rainbow trout and walleye were fed their regular stock-tank diets on the first and third days of the 5 day acclimation regime.

After the five day acclimatory period, Daphnia representing all free swimming stages were added to the pH 6.0 and pH 7.0 columns. Columns of the pH 6.0 treatment received 6.0 g (wet weight) of the Daphnia while columns of the pH 7.0 treatment received 3.0 g. No Daphnia were placed in the pH 5.0 column as they would not survive.

Each experimental column was sampled for chlorophyl a content prior to dosing with methylmercury²⁰³. Chlorophyl a determinations followed the spectrophotometric technique (Trichromatic Method) outlined in Rand *et al.*, 1976. Optical densities were measured on a PYE UNICAM SP1800 spectrophotometer.

Columns were dosed with stock solutions of methylmercury²⁰³ to effect a water concentration of approximately 4 ng/L. This concentration has been shown to approximate "natural" background concentrations (Norstrom and Brounstein, 1974). The CH₃Hg²⁰³ stock solution was injected by syringe and capillary tubing into the intake pipe of the column recirculation system. The dosing apparatus was rinsed many times to ensure complete isotope delivery.

Water samples (5 mL) were taken at 0 and 2, 4, 6, 24, 48, 72, 96 and 120 hours after isotope addition to monitor the fate of methylmercury²⁰³ in the columns during the experiment. Samples were counted in a Nuclear Chicago gamma scintillation counter (Model No. 18725) equipped with a sodium iodide crystal and a 3.18 cm sample well.

Uncontaminated distilled water in standard glass gamma counting tubes was used to estimate background levels of radiation. The background radiation count was taken as the mean counts per minute observed over nine minutes of monitoring.

Water samples were compared to previously prepared standard solutions. The 5 mL sample volume proved to be the most efficient quantity as it would completely fill the counting well when placed in standard glass gamma counting vials. These vials were used for all water samples. Each water sample was counted for one minute nine separate times, whereas standards were counted three times for one minute each. The mean number of background counts was calculated for these data. Calculation of methylmercury²⁰³ activity was related to a time 0 which represents the assay day of isotope as defined from the decay of the standard solutions.

During the course of the experimental period dissolved oxygen was monitored with a YS1 dissolved oxygen meter calibrated against a Winkler standard (Rand *et al.*, 1976). Dissolved oxygen was typically above 75% saturation.

Adjustments in pH and water temperature were made as required. Generally, water temperatures remained relatively constant ($18 \pm 1^\circ\text{C}$), while pH values were ± 0.3 pH units for each treatment.

Twenty-four hours after dosing, approximately 20 Daphnia magna were sampled from each pH 6.0 and pH 7.0 column. The Daphnia were placed in Bouins fixative (Humason, 1972), and counted for mercury²⁰³ activity. Sample activity was assessed from the mean of nine one minute counts. Phytoplankton samples were also taken at this time and processed for autoradiographical localization of methylmercury²⁰³. Subsequent to plankton sampling, rainbow trout were released to forage ad libitum on Daphnia in the columns.

Walleye feeding was initiated forty eight hours after addition of the methylmercury²⁰³ isotope to the columns and was repeated at seventy two and ninety six hours. The feeding procedure is described below:

- "Hot fed" walleye from the pH 6.0 and pH 7.0 treatments were fed with rainbow trout netted from their respective columns. "Hot fed" walleye in the pH 5.0 treatment were fed with rainbow trout netted from the pH 6.0 column. All "Hot" rainbow trout were weighed, counted for mercury²⁰³ activity in vivo and subsequently fed alive to the walleye. Counting rainbow trout in vivo was achieved by placing the fish head down in a standard gamma counting tube with 5 mL of well oxygenated fresh water and counting for one minute. After each counting, the trout were placed in a holding container with a larger volume of aerated water to recover from the stress of counting. The mean of three one minute counts was taken to represent in vivo isotope activity.
- "Cold fed" walleye in all pH treatments were fed with rainbow trout from stock tanks which were not exposed to the isotope. These fish were not monitored for Hg²⁰³ as preliminary countings on selected fish yielded similar counts as observed for

background levels. The exposure of "starved" walleye to Hg^{203} was limited to the ambient water in the individual columns.

After 120 hours of column dosing all walleye were sacrificed with an overdose of MS 222 (ethyl m-aminobenzoate methanesulfonate). Fish were subsequently weighed and then homogenized with a polytron tissue grinder. A weighed aliquot of the tissue homogenate (approximately 1 g), was placed in a counting tube and digested in 3 mL of 10% potassium hydroxide (KOH). Sample counts were taken as the mean of three one minute counts. The remainder was frozen (-20°C) and forwarded to MOE for tissue analysis of total mercury content.

Analysis of variance (ANOVA) and Duncan's comparison of means tests were performed on an APL computer (University of Guelph) on methylmercury²⁰³ uptake in walleye as a function of pH and feeding regime.

The ambient uptake of methylmercury²⁰³ by rainbow trout over a 120 hour period was investigated under exposure to pH 6.0 and 7.0 in a separate experiment. For this experiment, 6 rainbow trout were divided equally between the pH 6.0 and 7.0 columns of experimental replicate 3.

These fish were retained in cages but were not permitted to feed. Trout were removed after 24, 48, 72, 96 and 120 hours and counted *in vivo* as described previously. Methylmercury²⁰³ uptake from the diet was approximated from those fish which were feeding on Daphnia exposed to methylmercury²⁰³ after 48, 72 and 96 hours.

Analyses of variance (ANOVA), covariance (ANOCOVA), Student t-test, and regression were performed on APL computer (University of Guelph).

Autoradiography

Five hundred mL samples of phytoplankton were taken from the columns 24 hours after dosing with methylmercury²⁰³ and processed based upon the methods described by Knoechel and Kalff (1976). The samples were agitated to disperse the phytoplankton homogeneously and a 15 mL aliquot from each sample was transferred to a 20 mL centrifuge tube. Each sample was centrifuged for 2 minutes at 500 rpm. A 10 mL aliquot of the supernatant was decanted off and replaced with 10 mL of tap water. The tubes were shaken to disperse the phytoplankton, and then centrifuged again for 2 minutes at 500 rpm. This procedure was repeated four times to remove water borne Hg^{203} . Following the final rinse, all but 2 mL of the supernatant was decanted off and an aliquot of the remaining 2 mL was placed on acid cleaned slides and allowed to air dry. Air drying was preferred as it was less likely to cause rupture or deformation of the cell walls. Drying slides were placed in dust free boxes and were covered with a fine mesh phytoplankton webbing to prevent excess dust settling on the sample. When dry, the slides were placed in dust free dry microscope slide boxes and stored in preparation for autoradiographical localization of Hg^{203} .

Specimens of Daphnia magna were sampled from the experimental columns 24 hours after dosing with Hg^{203} . These specimens were preserved in Bouin's fixative until processed for autoradiography (Humason, 1972). The fixed Daphnia were rinsed of the Bouin's solution, dehydrated in an alcohol series, taken through xylene and finally embedded in paraffin wax following the methods of Humason (1972).

Embedded specimens were sectioned with a microtome to a thickness of 7 μ . Sections were placed on clean albuminised slides and allowed to dry. Wax was removed with xylene followed by hydration to water through an alcohol and water series (Humason, 1972). Sections were then stored in dry, dust free boxes until processed for the autoradiographical localization of Hg^{203} .

After appropriate preparation, slides of plankton specimens were dipped in Kodak Nuclear Emulsion NTB3. The thickness of the emulsion layer varied for phyto and zooplankton. The emulsion was much thicker on the slides of the phytoplankton types since track autoradiographs of Hg^{203} emissions from specific cells were desired. In the case of the zooplankton, the intention was to localize the Hg^{203} in various Daphnia tissues where grain density autoradiography is more aptly suited. Slide boxes were stored in a refrigerator and held at approximately 4°C while the latent image developed (Humason, 1972).

Slides were removed at varying intervals and developed according to Humason (1972). After development, zooplankton slides were stained with methyl green and pyronin (Humason, 1972). Staining was not required for phytoplankton slides.

Individual slides from all experimental groups were examined and representative photographs of plankton for each pH treatment were taken with a Zeiss photomicroscope (Model #4357006).

RESULTS

Lake Selection

Atkins, Wood and Walker Lakes were selected as the experimental lakes, their locations are shown in Figure 1.

Atkins, Wood and Walker Lakes displayed pH ranges of 5.30-7.02, 6.5-7.0 and 5.90-7.25, respectively (Table 1). The concentrations of heavy metals (Table 1) in these lakes were representative of uncontaminated lake waters (EPA, 1976; Enk and Mathis, 1977; Atchison *et al.*, 1977).

Acid Toxicity to Daphnia

As pH decreased, the mortality of Daphnia increased. The presence of food (Chlorella vulgaris), however, reduced the mortality in a given pH treatment. Experimental pH values during the bioassay were 5.32, 6.31 and 7.12. The trend to increasing mortality with a decrease in pH was maintained in both the fed and starved groups of Daphnia. No individuals survived exposure at pH 5.32 although the mortality rate was more rapid for starved animals. After 192 hours, none of the starved Daphnia survived exposures to pH 6.31 while an attendant mortality of 60% was observed for grazing Daphnia. Near total mortality (84%) of starved Daphnia occurred at pH 7.0 while the rate was much lower for feeding animals (4%).

Background Mercury Levels in Trout and Walleye

Mercury levels in trout and walleye were similar to those in uncontaminated fish (Reeder *et al.*, 1979) and were below the Ontario Ministry of the Environment's (MOE) Standard of 0.5 $\mu\text{g/g}$ Hg. The mean concentrations (wet weight) of these replicates for the two rainbow trout sampled were 0.006 and 0.005 $\mu\text{g/g}$ Hg and for the single walleye was 0.11 $\mu\text{g/g}$ Hg. Corresponding dry weight concentrations were 0.043 and 0.03 $\mu\text{g/g}$ Hg (trout) and 0.06 $\mu\text{g/g}$ Hg (walleye).

Methylmercury²⁰³ Uptake Through the Simulated Ecosystems

Upon dosing, methylmercury²⁰³ rapidly distributed throughout the columns and was detectable in surface waters two hours after addition. Final concentrations in the column (\pm one standard deviation) were 2.99 ± 0.54 , 2.54 ± 2.01 and 2.35 ± 0.44 for pH treatments of 5.0, 6.0 and 7.0 respectively.

Algal biomass estimates of column water taken just prior to isotope dosing appear to indicate a trend toward lower algal biomass with increasing acidity (Figure 2).

These biomasses were, however, adequate to sustain Daphnia in the columns for 96 hours based on a daily requirement of 10% of the total Daphnia biomass (wet weight).

Methylmercury²⁰³ was accumulated by Daphnia magna after 24 hours exposure in the column at pH 6.0 and 7.0 (Table 2). It appears that a greater amount of methylmercury²⁰³ is accumulated at pH 7.0 which exhibited a mean concentration per individual of 0.064 μg compared with

FIGURE 1
LOCATION OF EXPERIMENTAL LAKES

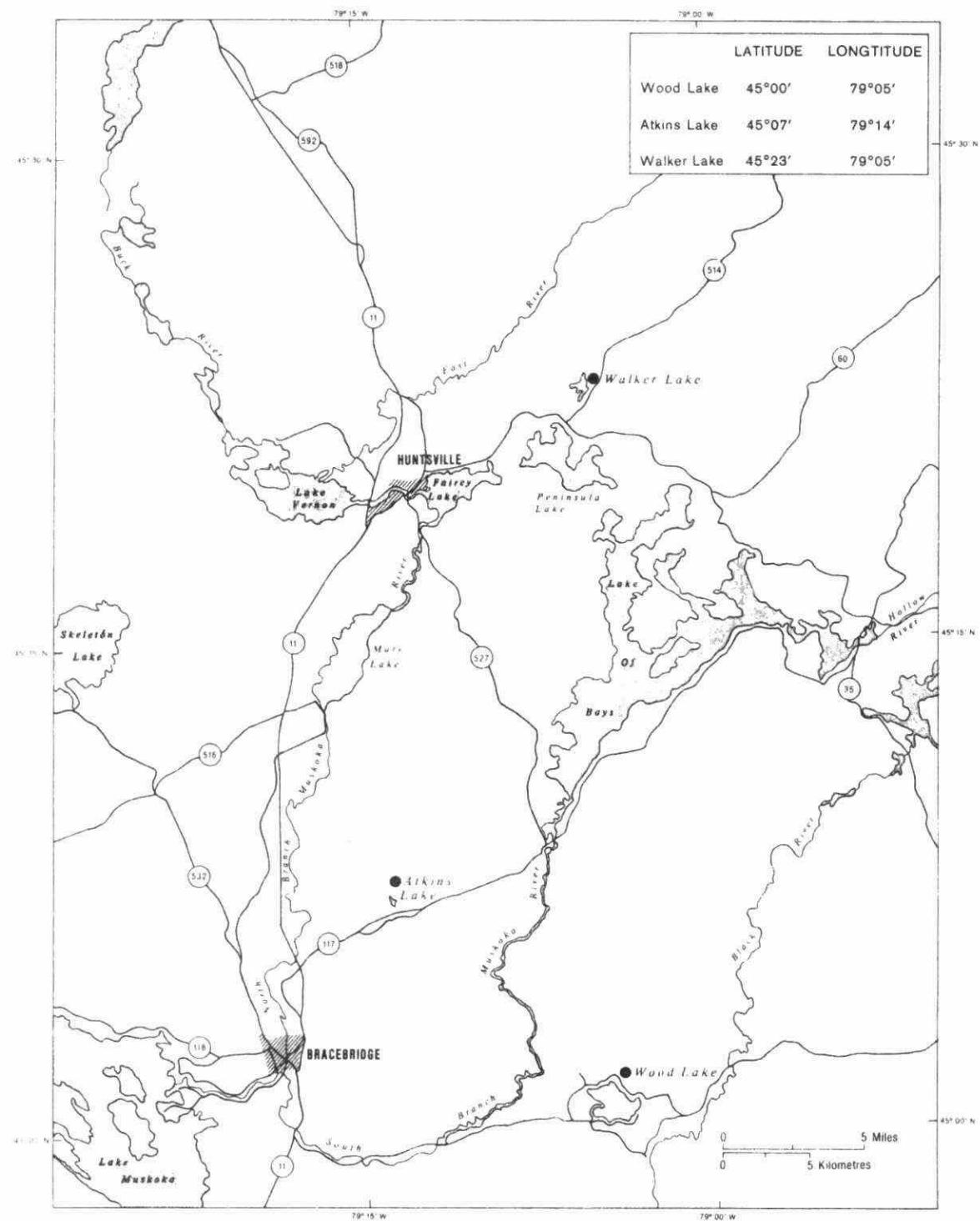


TABLE 1
CHEMICAL PARAMETERS OF SELECTED LAKES

Lake	pH	CCIW	Enviro- clean	Total Dissolved Metals (mg/L)					Hardness CaCO ₃ (mg/L)	Total Dissolved Solids (mg/L)
				MOE	Cadmium	Copper	Lead	Mercury		
Atkins	5.95	7.20		5.30	<0.005	<0.02	<0.02	<0.1	<0.01	5.50
Walker	6.50	6.70		6.75	<0.005	<0.02	<0.02	<0.1	<0.01	7.00
Wood	6.70	6.80		5.90	<0.005	<0.02	<0.02	<0.1	<0.01	7.75

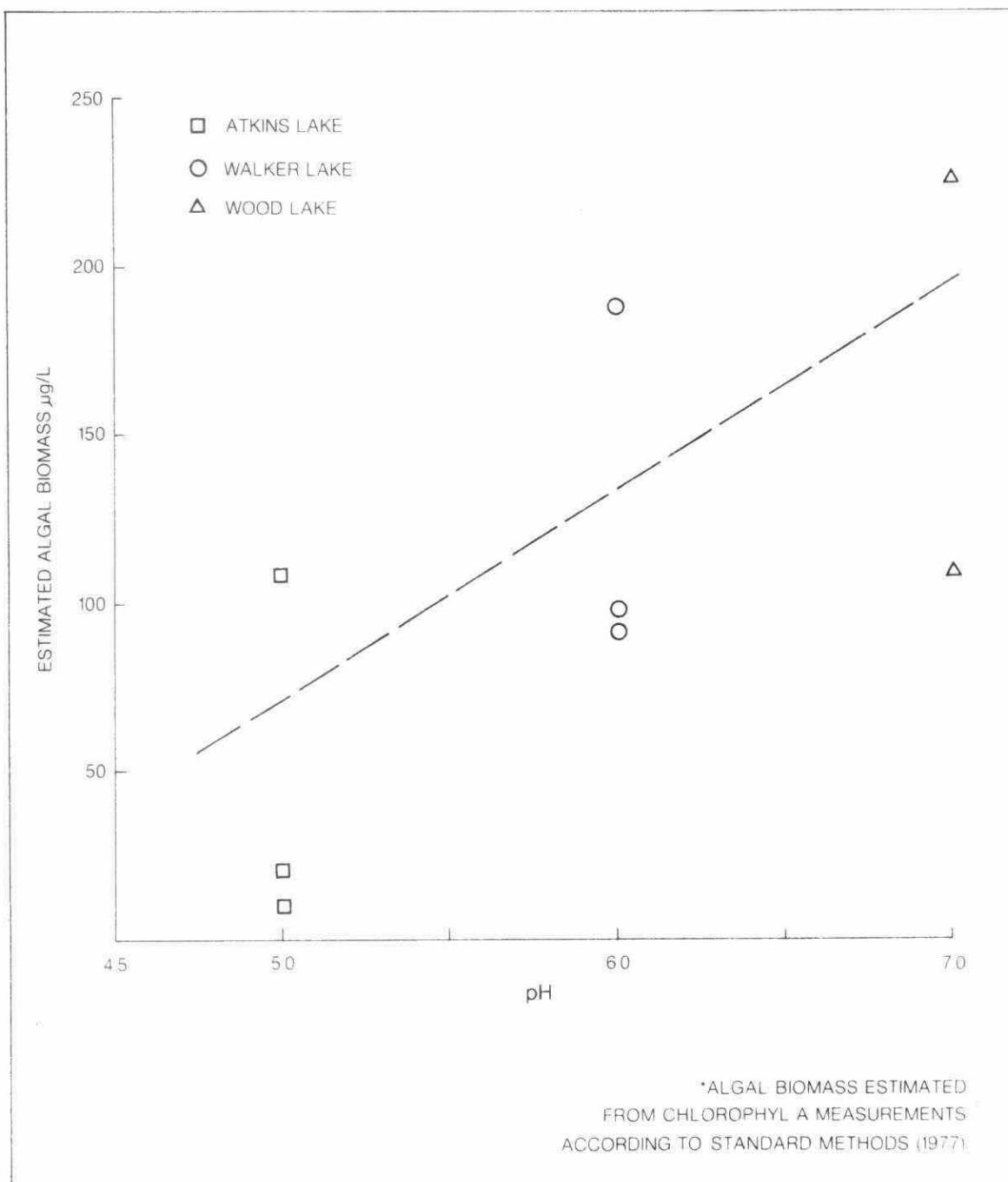
TABLE 2

CONCENTRATION OF METHYLMERCURY²⁰³ IN
Daphnia magna AFTER TWENTY-FOUR HOURS

Treatment	Replicate No.	No Individuals	Total CH ₃ Hg ²⁰³ (ng)	CH ₃ Hg ²⁰³ Individual	Mean
pH 5.0	(No surviving <u>Daphnia magna</u> at this pH)				
pH 6.0	R1	20	0.583	0.029	0.037
	R2	15	0.656	0.042	
	R3	20	0.820	0.041	
pH 7.0	R1	50	1.226	0.053	0.064
	R2	20	0.575	0.030	
	R3	20	2.200	0.110	

FIGURE 2

RELATIONSHIP OF pH AND COLUMN ALGAL BIOMASS*
AT EXPERIMENT INITIATION AFTER NINE DAYS
EXPOSURE TO EXPERIMENTAL pH REGIMES



0.037 μ g at pH 6.0. Data for methylmercury²⁰³ accumulation in Daphnia at pH 5.0 were not available as this pH regime was shown to be acutely lethal to the zooplankter.

Total concentrations of methylmercury²⁰³ in feeding rainbow trout after 48, 72 and 96 hours at pH 6.0 and 7.0 are presented in Table 3.

The cumulative methylmercury²⁰³ concentrations after 96 hours (sum of 48, 72 and 95 hour levels) in trout are different ($P<0.01$, Student's t-test). The cumulative concentration (ng/g) of methylmercury²⁰³ in trout at pH 7.0 ($\mu = 26.83$ ng/g) was 65% greater than the level at pH 6.0 ($\mu = 16.25$ ng/g).

Concentrations of methylmercury²⁰³ over time for trout at pH 6.0 and 7.0 and under different feeding regimes (Table 4, Figure 3) were different ($P<0.05$; ANOCOVA). Trout from pH 7.0 treatments had higher methylmercury²⁰³ levels compared with those from pH 6.0 while feeding trout had higher concentrations than starved fish.

The total amount of methylmercury²⁰³ assimilated by walleye through prey (rainbow trout) is summarized in Table 5. No differences ($P>0.05$, ANOVA) were observed in the amount of methylmercury²⁰³ accumulated by walleye in the different pH regimes. A significant ($P<0.05$, ANOVA) feeding effect was, however, observed. Duncan's comparison of means test showed the mean methylmercury²⁰³ concentration of walleye (1.26 ng/g) fed with labelled trout was greater than from the mean of starved walleye (0.60 ng/g) as well as those fed (0.71 ng/g) with unlabelled rainbow trout. The latter two groups of walleye were similar in their methylmercury²⁰³ content ($P>0.05$, ANOVA).

The ultimate concentrations of methylmercury²⁰³ in individual walleye and rainbow are summarized in Table 6. These data were used to compare the amount of methylmercury²⁰³ retained by walleye after having been fed with labelled trout. There were no differences ($P>0.05$, ANOVA) in the amount of methylmercury²⁰³ accumulated or eliminated by walleye. The approximate percentage retained for walleye in all pH treatments was 8.00 with the remainder being eliminated.

Mercury Levels in Post Experimental Walleye

There was no significant difference ($P>0.05$, ANOVA) in the Hg concentrations of walleye between replications in a given pH group nor between similar feeding regimes of the various pH treatments. The range of Hg concentrations (mean \pm standard deviation) were from 0.11 ± 0.01 to 0.13 ± 0.03 μ g/g (wet weight).

FIGURE 3

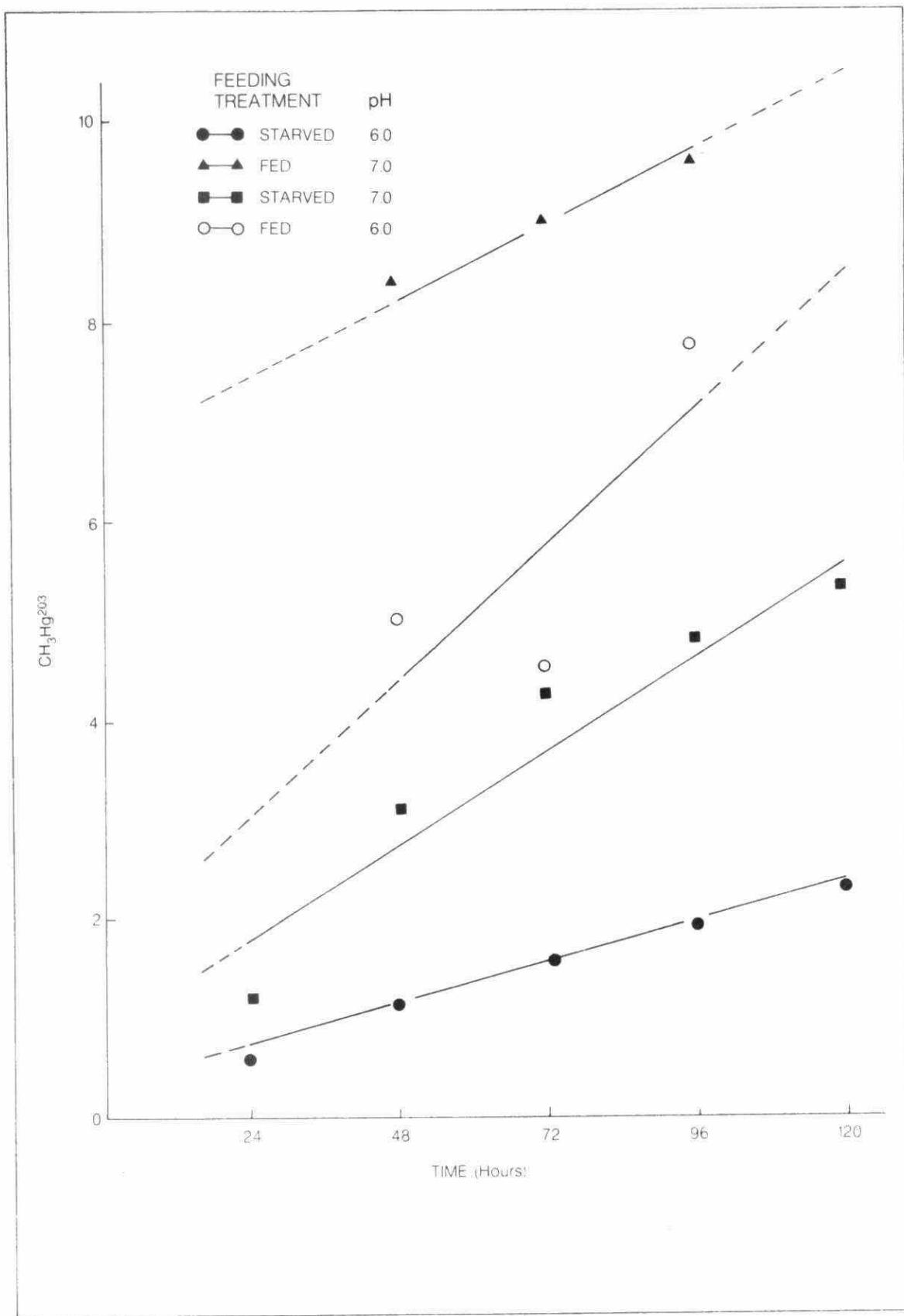
RELATIONSHIP OF MEAN MERCURY UPTAKE (ng/g) WITH pH
AND FEEDING REGIME IN RAINBOW TROUT (*Salmo gairdneri*)

TABLE 3

METHYLMERCURY²⁰³ CONCENTRATIONS IN RAINBOW TROUT (ng/g)
AT VARIOUS WALLEYE FEEDING TIMES (hours) and pH TREATMENTS

Replicate	Fish	pH 5.0*				pH 6.0				pH 7.0			
		48h	72h	96h	Sums	48h	72h	96h	Sums	48h	72h	96h	Sums
R1	1	3.04	5.58	6.33	14.95	4.46	5.91	7.42	17.79	12.87	1.08	5.73	19.68
	2	3.72	3.78	5.70	13.20	3.01	2.92	1.31	9.24	10.04	11.99	11.21	33.24
	3	3.33	4.61	4.82	12.76	4.29	5.01	-	9.30	8.14	7.42	7.56	23.12
R2	1	3.76	5.79	8.87	18.42	4.84	5.69	10.47	21.00	11.21	2.13	2.38	15.72
	2	4.54	5.96	17.34	27.84	3.61	4.89	5.51	14.01	1.51	3.29	3.34	8.14
	3	3.18	4.87	3.42	11.47	12.23	3.17	17.45	32.85	3.91	1.34	3.39	8.64
R3	1	4.54	6.55	8.34	19.43	2.70	3.96	5.47	12.13	10.51	8.37	28.75	47.63
	2	4.81	7.40	4.24	16.45	6.28	4.16	6.84	12.28	9.41	15.45	10.95	35.81
	3	4.91	4.90	5.46	15.27	4.23	4.92	-	9.15	5.70	30.56	13.29	49.55
Means		16.64				15.86				26.84			

NOTE: Mean values 16.64 and 15.86 ng/g methylmercury²⁰³ were average ($\frac{16.64 + 15.86}{2} = 16.25$) and represent the total amount of methylmercury²⁰³ accumulated by rainbow trout at pH 6.0.

* Trout were actually exposed to methylmercury²⁰³ at pH 6.0, then fed to pH 5.0 walleye.

TABLE 4
METHYLMERCURY²⁰³ UPTAKE IN FED AND STARVED RAINBOW TROUT

Feeding Regime	pH	Concentrations Over Time (ng/g)				
		24h	48h	72h	96h	120h
Starved n = 3	6.0	0.52	1.06	1.41	1.73	1.91
		0.77 (0.60)	1.74 (1.29)	2.06 (1.62)	2.52 (1.96)	2.66 (2.15)
		0.50	1.06	1.39	1.63	1.87
Starved n = 3	7.0	0.90	2.13	2.95	3.83	4.67
		1.36 (1.23)	1.81 (3.16)	2.54 (4.30)	2.92 (4.83)	3.26 (5.38)
		1.42	5.54	7.41	7.75	8.22
Fed n = 9	6.0	-	4.46	5.91	7.42	-
		-	3.01	2.92	1.31	-
		-	4.29	5.01	-	-
		-	4.84	5.69	10.47	-
		-	3.61 (5.07)	4.89 (4.51)	5.51 (7.78)	-
		-	12.23	3.17	17.45	-
		-	2.70	3.96	5.47	-
		-	6.28	4.16	6.84	-
		-	4.23	4.92	mortality	-
		-	-	-	-	-
Fed n = 9	7.0	-	12.87	1.08	5.73	-
		-	10.04	11.99	11.21	-
		-	8.14	7.42	7.56	-
		-	11.21	2.13	2.38	-
		-	1.51 (8.14)	3.29 (9.07)	3.34 (9.62)	-
		-	3.91	1.34	3.39	-
		-	10.51	8.37	28.75	-
		-	9.41	15.45	10.95	-
		-	5.70	30.56	13.29	-
		-	-	-	-	-

TABLE 5

METHYLMERCURY²⁰³ CONCENTRATIONS IN WALLEYE (ng/g)
AFTER 120 HOURS EXPOSURE

Feeding Regime	pH 5.0		pH 6.0		pH 7.0	
	obs.	means	obs.	means	obs.	means
R1	H1	1.00		1.01		1.02
	H2	0.79	H = 0.85	0.61	H = 0.67	0.89
	H3	0.77	C = 0.36	0.38	C = 0.69	0.99
	C1	0.33	S = 0.27	0.72	S = 0.65	0.38
	C2	0.38	$\bar{\epsilon}$ = 0.49	0.65	$\bar{\epsilon}$ = 0.68	0.48
	C3	0.36		0.69		0.57
	S1	0.27		0.61		0.58
	S2	0.27		0.72		0.48
	S3	0.28		0.62		0.44
R2	H1	1.34		1.13		1.82
	H2	1.08		1.18		1.75
	H3	0.82	H = 1.08	1.41	H = 1.24	1.51
	C1	0.65	C = 0.63	0.81	C = 0.75	1.14
	C2	0.63	S = 0.54	0.66	S = 0.60	1.02
	C3	0.60	$\bar{\epsilon}$ = 0.75	0.78	$\bar{\epsilon}$ = 0.86	1.07
	S1	0.55				0.81
	S2	0.52				0.81
	S3	0.54				0.66
R3	H1	2.31		1.12		1.29
	H2	2.06	H = 2.18	1.47	H = 1.39	1.22
	H3	2.17	C = 0.73	1.59	C = 0.99	1.14
	C1	0.70	S = 0.67	1.15	S = 0.87	0.68
	C2	0.59	$\bar{\epsilon}$ = 1.19	0.99	$\bar{\epsilon}$ = 1.08	0.63
	C3	0.91		0.83		0.79
	S1	0.75		0.74		0.66
	S2	0.64		0.93		0.52
	S3	0.61		0.94		0.56

Overall means from feeding regardless of pH.

"Hot fed" = 1.26

"Cold fed" = 0.71

"Starved" = 0.60

TABLE 6

METHYLMERCURY²⁰³ UPTAKE BY WALLEYE FROM METHYLMERCURY²⁰³ EXPOSED RAINBOW TROUT
(ng/g)

pH	Replicate No.	Walleye	Rainbow Trout	Percent Retained by Walleye	Percent Eliminated by Walleye
5.0	1	1.00	14.95	7.0	93.0
	1	0.79	16.75	5.0	95.0
	1	0.77	12.76	6.0	94.0
	2	1.34	18.42	7.0	93.0
	2	1.08	27.84	4.0	96.0
	2	0.82	11.47	7.0	93.0
	3	2.31	19.43	12.0	88.0
	3	2.06	16.45	13.0	87.0
	3	2.17	15.27	14.0	86.0
				Mean = 8.33	Mean = 91.67
6.0	1	1.07	17.79	6.0	94.0
	1	0.61	7.24	8.0	92.0
	1	0.38	9.30	5.0	95.0
	2	1.13	21.00	5.0	95.0
	2	1.18	14.01	8.0	92.0
	2	1.41	32.85	4.0	96.0
	3	1.12	12.13	9.0	91.0
	3	1.47	17.28	9.0	91.0
	3	1.59	9.15	17.0	83.0
				Mean = 7.88	Mean = 92.11
7.0	1	1.02	19.68	5.0	95.0
	1	0.89	32.24	3.0	97.0
	1	0.99	23.12	4.0	96.0
	2	1.82	15.72	12.0	88.0
	2	1.75	8.14	21.0	79.0
	2	1.51	8.64	17.0	83.0
	3	1.29	47.63	3.0	97.0
	3	1.22	35.81	3.0	97.0
	3	1.14	49.55	2.0	98.0
				Mean = 7.78	Mean = 92.22

Autoradiography

Methylmercury²⁰³ is apparently taken up by phytoplankton as is shown in Figure 4. In this autoradiogram a track emission is evident in an individual phytoplankton from pH 5.0 at the 3 o'clock position. Phytoplankton in other pH regimes also appear to incorporate methylmercury²⁰³. Although methylmercury²⁰³ is taken up by some algae, others show no evidence of track emissions or overlying silver grains (Figure 5). This specimen was exposed to 4 ng/L methylmercury²⁰³ for 24 hours at pH 7.0.

Direct counting of Daphnia magna for methylmercury²⁰³ showed that the isotope was accumulated by the animals at pH 6.0 and 7.0 with those of the latter regime exhibiting a greater concentration. Processed autoradiograms, however, failed to show any localization of silver grains overlying histological sections of the same Daphnia magna specimens.

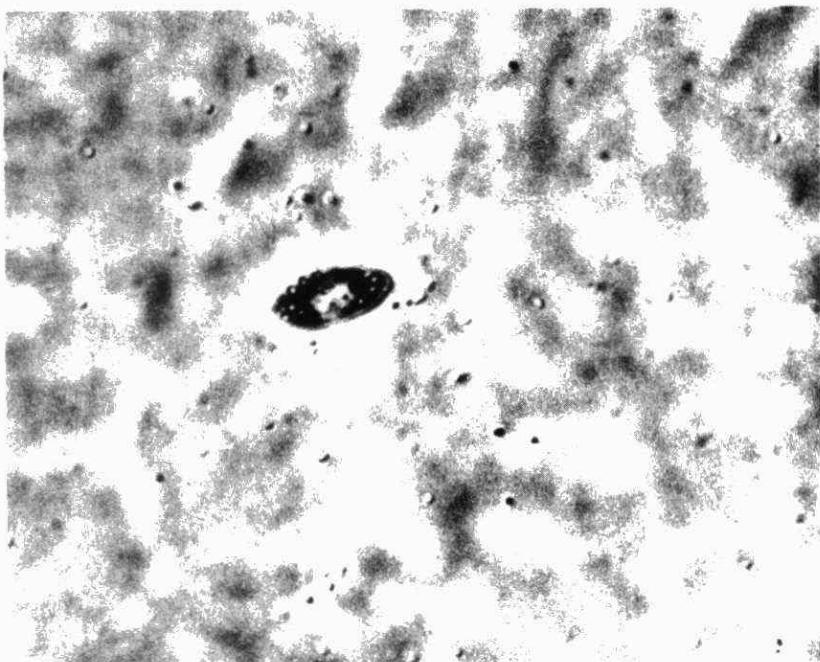


FIGURE 4

ONE PHYTOPLANKTER WITH ONE TRACK EMISSION AND
A FEW OVERLYING SILVER GRAINS AFTER 24 HOUR EXPOSURE
TO 4 ng/L METHYLMERCURY ²⁰³ AT pH 5.0.
MAGNIFICATION, 635x.

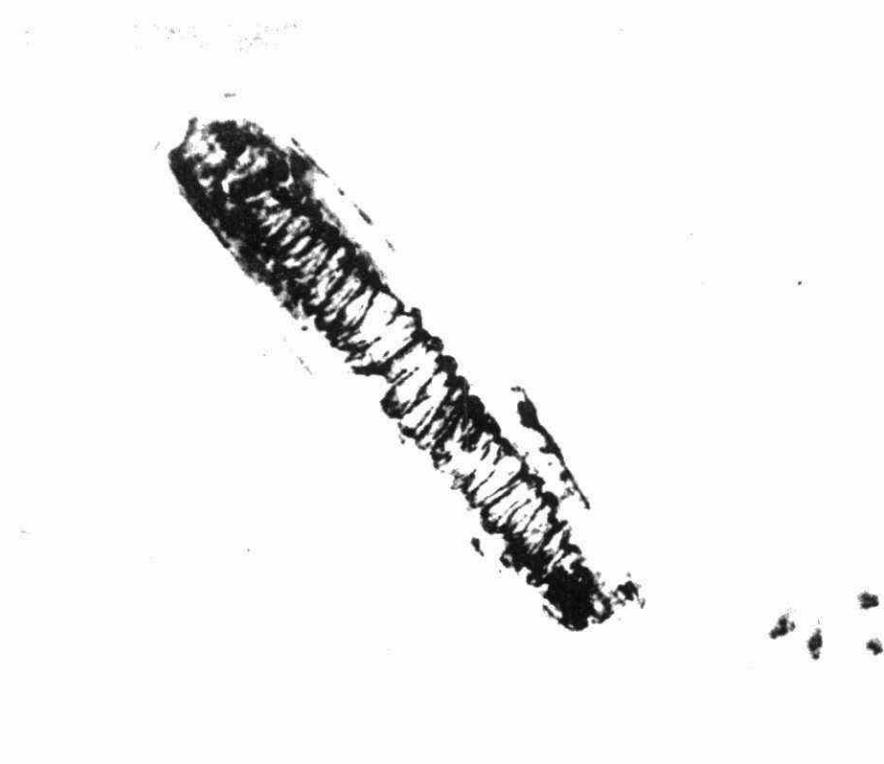


FIGURE 5

A NON-RADIOACTIVE PHYTOPLANKTER AS EVIDENCED
BY THE LACK OF SILVER GRAINS AND TRACK EMISSIONS
AFTER 24 HOURS EXPOSURE TO 4 ng/L METHYLMERCURY²⁰³
AT pH 7.0. MAGNIFICATION, 367x.

DISCUSSION

Study Lakes

The selected study lakes (Atkins, Walker and Wood) are all found in the Muskoka region of Ontario. Although these lakes are not considered to be under acid-stress at the present time they display similar physical and chemical parameters as lakes that may be affected by acid precipitation. Total dissolved solids in these lakes varied from 20-30 mg/L and are comparable with the range of values (10-49 mg/L) for lakes in the La Cloche Mountains of Ontario which are undergoing acidification (Beamish and Harvey, 1972; Beamish, 1974; Beamish *et al.*, 1975). The range of hardness values (5.50 to 7.75 mg/L as CaCO_3) for the three study lakes was slightly lower than the range (7.92 to 16.30 mg/L as CaCO_3) for lakes in the La Cloche Mountains. The pH ranges of Atkins, Walker and Wood (5.30 to 7.20; 6.50 to 6.75; 5.90 to 6.80; respectively) were, however, higher than the average of 4.6 for lakes within the La Cloche Mountains taken in 1971 (Beamish and Harvey, 1972).

The three study lakes at present appear to be oligotrophic. If acidic inputs continue, it is anticipated these lakes will become increasingly oligotrophic, similar to those in the La Cloche Mountains. The poor buffering capacity of the lakes is evidenced by the relatively small amounts of acid or base required for titration to the pH levels employed in this study. The three lakes selected for use in this study are, ostensibly, free from heavy metal contamination, as concentrations of certain heavy metals (cadmium, copper, lead, mercury and zinc) are all within the ranges reported for natural freshwater aquatic environments (EPA, 1976; Atchison *et al.*, 1977; Enk and Mathis, 1977). Generally, these concentrations were lower than those observed in acid-stressed lakes from similar geographical locations in Ontario (Beamish, 1974).

Acid Toxicity to Daphnia

Mortality rates of Daphnia magna increased markedly with a depression of pH. D. magna appears to be one of the more sensitive species in the genus as D. pulex were observed to tolerate a pH as low as 4.3 (Davis and Ozburn, 1969). The latter species, however, could not reproduce successfully below pH 7.0. The protective effect of food on the toxicity of pH in D. magna is not understood.

Mercury Levels and Uptake in Experimental Animals

Mercury content in the trout and walleye used for these experiments was very low. The range of concentrations in trout and walleye was from 0.002 to 0.012 $\mu\text{g/g}$ and from 0.003 to 0.016 $\mu\text{g/g}$ respectively, on a wet weight basis. These levels are well below the level of 5 $\mu\text{g/g}$ which is recommended as being safe for human consumption (EPA, 1976; Reeder *et al.*, 1979;).

Background concentrations of mercury from trout and walleye used in this study are representative of uncontaminated specimens. These levels correspond to amounts observed in uncontaminated fish from various aquatic environments (Aronson *et al.*, 1976; Abernathy and Cumbie, 1977; Brown and Chow, 1977; Lloyd *et al.*, 1977). Although only three trout and two walleye were used for analysis, it is presumed that similar low

levels of mercury were also present in the other fish comprising the stocks used for the experiment.

Assays for mercury content were not performed for Daphnia magna nor Chlorella vulgaris or the indigenous phytoplankton communities of the study lakes. Cultures of D. magna and C. vulgaris were assumed to contain very low levels of mercury as they were raised in relatively sterile laboratory conditions. It is unlikely that indigenous phytoplankton of the study lakes were contaminated with mercury in view of the relatively low background levels of the metal in the lake water.

Estimates of algal biomass or primary productivity by measurement of chlorophyll a content indicated a trend toward lower mean values with increasing acidity. These observations were, however, not statistically significant (ANOVA, $P < 0.05$). An apparent decrease in primary productivity as well as a reduction in the diversity of phytoplankton communities has been reported as a result of increased acidity (Kwiatkowski and Roff, 1976). Yan et al., (1977) suggest, however, that algal biomass does not significantly decrease in acid lakes. Although insignificant, the trends observed in this study contradict the suggestion of Yan et al. (1977). More precisely designed laboratory experiments may provide further insight into the ultimate elucidation of the problem.

Daphnia magna could not be cultured at pH values lower than 7.0. This observation is consistent with that reported for D. pulex, a species which also cannot reproduce at pH 5.0 and 6.0 (Davis and Ozburn, 1969). Both species, however, can tolerate pH levels below those of neutrality.

Methylmercury²⁰³ uptake by D. magna was monitored at pH 6.0 and 7.0. Uptake data are, however, not available at pH 5.0 as this acid regime was shown to be lethal to the experimental animals. After 24 hour exposure to methylmercury²⁰³, significant accumulations of the compound had taken place. Daphnia exposed to methylmercury²⁰³ at pH 7.0 accumulated approximately 1.7 times as much methylmercury²⁰³ compared with Daphnia at pH 6.0. Huckabee et al. (1975) and Lock (1975) also reported that Daphnia sp. accumulate Hg very rapidly. The differences between the content of Daphnia at pH 6.0 and 7.0 after 24 hours may not relate to the levels accumulated after longer term exposures since the equilibrium concentration of methylmercury is usually not acquired until after 6 days of exposure to the metal (Huckabee et al., 1975). Differences in uptake between Daphnia at the two pH exposures may, however, be related to metabolic rate, feeding behaviour or some other factor. Daphnia at neutral pH would probably be respiring and feeding at rates typical of healthy individuals. Exposure to the lower pH treatment (pH = 6.0) may have caused an alteration of respiration rate or feeding behaviour which may have ultimately affected the amount of methylmercury²⁰³ being accumulated. One could perceive, for example, that acid exposure might depress appetite in Daphnia thus precluding methylmercury 203 accumulation to the same extent or greater as normally feeding individuals.

There were a few apparent erroneous estimates of methylmercury²⁰³ concentration in the ecosystem columns but these measurements could not have explained the differences in the quantity of methylmercury²⁰³ in Daphnia exposed to the metal at pH 6.0 and 7.0. The accumulation of Hg by Daphnia as a function of pH should be investigated more thoroughly as

it may be affecting metabolic rate, feeding behaviour, excretion, or a number of other life processes.

Although direct measurements of methylmercury²⁰³ in Daphnia magna showed the isotope was readily taken up, autoradiographs failed to show any localization of silver grains that could be attributed to the isotope. In this study, Kodak NTB₃ nuclear emulsion was used to detect the localization of the CH₃ Hg²⁰³ as atoms of Hg²⁰³. It would appear that NTB₃ nuclear emulsion would be adequate for localization of Hg²⁰³ as the emulsion can record β particles at minimum ionization (Rogers, 1973). Rogers (1973) indicates, for example, that Kodak NTB₃ nuclear emulsion will record β particles of any energy including those at minimum ionization. This would include, of course, Hg²⁰³ which has a β particle emission at 0.20 MeV. The lack of silver grains in the Daphnia autoradiographs may be related to development time. The specific activity of the Hg²⁰³ label in the Daphnia may have required longer periods of development than the time regimes used in the current study.

Track autoradiography of Hg²⁰³ in phytoplankton clearly indicated that methylmercury²⁰³ was incorporated by algae. Phytoplankton autoradiographs employed a thicker emulsion layer compared with those for Daphnia. In track autoradiographs, the passage of a beta particle is recorded as a string of silver grains as shown in Figure 4. Not all phytoplankton, however, exhibited track emissions (Figure 5). The apparent absence of the isotope from certain algae may suggest that particular species have a greater affinity for the element or that inherent species differences are reflective of differential accumulation factors.

Methylmercury²⁰³ uptake by rainbow trout was greater in fed fish exposed to the isotope at pH 7.0 compared with fish at pH 6.0. Trout accumulated significantly more methylmercury²⁰³ at pH 7.0 than 6.0. Walleye feeding on the former group were obviously presented with greater total amounts of methylmercury in their diet. The relative importance of food and diet on methylmercury uptake in trout is apparent from perusal of Figure 3. Approximately 2 to 3 times more methylmercury²⁰³ was accumulated by fish that were fed at both pH 6.0 and 7.0 compared with starved fish. Comparisons of methylmercury²⁰³ content in "fed" and "starved" trout indicated that 70.6% and 44.1% of the total amount of methylmercury²⁰³ accumulated by trout at pH 6.0 and 7.0, respectively, was due to ingestion. The latter estimation of food's contribution to total mercury levels agrees well with observations from other studies (Hannerz, 1968; Huckabee *et al.*, 1975; Norstrom *et al.*, 1976; Phillips and Buhler, 1978). A figure of 44.1% for trout at pH 7.0 is interesting and may suggest that uptake via water is more significant at higher pH. It may not be coincidence, therefore, that trends toward lower methylmercury²⁰³ levels were observed at pH 7.0 compared with columns at pH 5.0 and 6.0. In a study with inorganic mercury, Tsai *et al.* (1975) found, however, that the uptake of mercury by fathead minnows increased sharply at pH values below 7.0. They interpreted their observations as being due to the formation of less reactive mercury hydroxide complexes at the higher pH regimes. In the current study, the mercury was in the form of methylmercury and, hence, the formation of hydroxide complexes at more alkaline pH regimes was likely precluded. The uptake dynamics of inorganic mercury cannot, therefore, be compared to those of methylmercury at similar pH levels.

The mechanism by which pH effects mercury uptake by fish is not clear. It is suggested that an unidentified metabolic parameter is contributing to the enhanced uptake of methylmercury²⁰³ at pH levels near neutrality. This parameter may be related to reduced elimination rates and/or increased uptake of the isotope from the food or water.

Under field conditions, fish in acid-stressed environments have exhibited enhanced tissue levels of methylmercury (Landner and Larsson, 1972, Suns *et al.*, 1980). Intuitively, one would have expected to verify such observations experimentally but the results of this study have yielded data contrary to this hypothesis.

Miller and Akagi (1979) have shown that the enhanced uptake of methylmercury by fish in acid-stressed environments is related to increased levels of the compound rather than a physiological response of the animals. They found, for example, that changing values of the pH in natural sediment-water systems did not affect the total amount of methylmercury generated in the sediments. They also observed that the partition of methylmercury between water and sediment did change with the amount of methylmercury in the water column; doubling for a decrease in pH of 1 or 2 units depending on sediment type. Miller and Akagi (1979) also indicated that these changes were enough to quantitatively explain the observed elevations in fish taken from lakes of low pH.

In the present study, rainbow trout were exposed to similar levels of methylmercury²⁰³ at three different pH regimes. As there was no sediment component in the simulated ecosystem columns the concentrations of methylmercury²⁰³ did not change in the water as a result of sediment methylation or repartitioning. Elucidation of the effects of methylmercury uptake by fish in low pH environments is somewhat confused by the results of this study in comparison with recent theories on the subject.

Unlike rainbow trout, walleye did not accumulate methylmercury²⁰³ differently with pH. Starvation did not affect the amount of methylmercury²⁰³ taken up from water, as walleye fed with unlabelled trout displayed a similar quantity of accumulated mercury. Walleye that were fed with methylmercury²⁰³ exposed trout accumulated roughly twice as much methylmercury²⁰³ as "starved" or "cold-fed" walleye. The contribution of methylmercury²⁰³ from food in walleye fed with methylmercury²⁰³ was roughly 50%. Jernelov (1970) reported similar data which suggested that 50% of the mercury in Swedish pike came directly from the water. These data do not contribute to the elucidation of the hypothesis that food is the greatest contributor to body-burden levels of mercury in exposed fish.

The relative percentage contribution of methylmercury²⁰³ by food observed for walleye in this study may have been underestimated. Methylmercury²⁰³ contaminated trout were exposed to the isotope for a maximum of 4 days prior to predation by walleye. This period of exposure may not have been adequate for methylmercury²⁰³ to reach an equilibrium in trout. Overall body burden levels in these fish may, therefore, have been lower compared with trout exposed to similar levels of methylmercury²⁰³ for prolonged periods under natural conditions. For this reason, the ultimate levels of methylmercury²⁰³ contributed by the trout may not have been as large if the trout had been exposed to the radioisotope for longer periods.

The percent of methylmercury²⁰³ retained or eliminated in walleye did not differ with pH and ranged from 7.78 to 8.33 percent and from 91.67 to 92.22 percent respectively. These retention data are somewhat less than the 41.6% figure observed for trout by Hamelink *et al.* (1975). In their study, however, the retention values represented data from fish that had been exposed to methylmercury for one year. Mercury uptake for walleye in this study may not have reached equilibrium in the relatively short exposure period of 4 days. The estimates presented for retention and elimination of methylmercury²⁰³ may, therefore, be erroneous. Huckabee *et al.* (1975) found for example, that the elimination of methylmercury²⁰³ from mosquito fish (*Gambusia affinis*) was greatest in the fish 5 days after feeding, dropping off to a relatively constant elimination rate after 20 days.

The maximum levels of mercury reported in walleye after the experiment were all well below the Environment Canada (Reeder *et al.* 1979) safe level of 0.5 $\mu\text{g/g}$. Final whole body concentrations on a wet weight basis ranged from 0.11 to 0.13 $\mu\text{g/g}$. Acidity did not affect the concentration of mercury in experimental fish nor did the feeding treatments. Concentrations of mercury in post experimental walleye were, however, about an order of magnitude higher compared with walleye that were analysed prior to the beginning of the experiments. This increase cannot be explained by the mercury accumulated from exposure to methylmercury²⁰³ since the walleye accumulated the isotope in less than 3 ng/g quantities at all pH treatments. An addition of 3 ng/g of mercury to pre-experimental mercury levels would be difficult to detect.

The data presented in this report show methylmercury's potential for movement and accumulation at various trophic levels of the aquatic ecosystem. Fish and zooplankton exposed to neutral pH regimes accumulate more methylmercury compared with animals exposed at more acid pH.

In the natural environment, however, the concentration of methylmercury is higher in acid-stressed fish. One must conclude that there are other factors contributing to the accumulation of methylmercury in these organisms, besides acidity. Water quality as well as mercury-methylation rates and concentrations, for example, are probably affecting the accumulation of the compound by fish in acid waters. Additional studies are required to increase the understanding of the dynamics of methylmercury uptake in fish especially from acid environments.

REFERENCES

Abernathy, A.R. and P.M. Cumbie. 1977. Mercury accumulation by largemouth bass (Micropterus salmoides) in recently impounded reservoirs. *Bull. Env. Contamin. and Toxicol.* 17(5):595-600.

Aronson, J.L., M. Spiesman and A.K. Aronson. 1976. Note on the distribution of mercury in fish species in three Ohio Lakes. *Environ. Pollut.* 10:1-7.

Atchison, G.J., B.R. Murphy, W.E. Bishop, A.W. McIntosh and R.A. Mayer. 1977. Trace metal contamination of bluegill (Lepomis macrochirus) from two Indiana Lakes. *Trans. Am. Fish. Soc.* 106:637-640.

Beamish, R.J. and H.H. Harvey. 1972. Acidification of the La Cloche Mountain lakes, Ontario and resulting fish mortalities. *J. Fish. Res. Bd. Canada* 29: 1131-1143.

Beamish, R.J. 1974. Loss of fish populations from unexploited remote lakes in Ontario, Canada as a consequence of atmospheric fallout of acid. *Water Rec.* 8:85-95.

Beamish, R.J., W.L. Lockhart, J.C. Van Loon and H.H. Harvey. 1975. Long-term acidification of a lake and resulting effects on fishes. *Ambio.* 4:98-102.

Brown, J.R. and L.Y. Chow. 1977. Heavy metal concentrations in Ontario fish. *Bull. Env. Contamin. Toxicol.* 17(25): 190-195.

Carter, J.C.H. 1971. Distribution and abundance of planktonic Crustacean in ponds near Georgian Bay (Ontario, Canada) in relation to hydrography and water chemistry. *Arch. Hydrobiol.* 68:204-231.

Craig, G.R. and W.F. Baksi. 1977. The effects of depressed pH on flagfish reproduction, growth and survival. *Water Res.* 11:621-626.

Davis, P. and S.W. Ozburn. 1969. The pH tolerance of Daphnia pulex (Leydig, emed., Richard). *Can. J. Zool.* 47:1173-1175.

Dillon, P.J., D.S. Jeffries, W. Snyder, R. Reid, N.D. Yan, D. Evans, J. Moss and W.A. Schneider. 1977. Acidic precipitation in south-central Ontario: recent observations. *Ont. Min. Environment.*

Enk, M.D. and B.J. Mathis. 1977. Distribution of cadmium and lead in a stream ecosystem. *Hydrobiologia* 52(2-3): 153-158.

EPA. 1976. Quality Criteria for Water. U.S. Environmental Protection Agency. EPA-440/9-76-023.

Hamelink J., R.C. Waybrant and P.R. Yant. 1975. Mechanisms of bio-accumulation of mercury and chlorinated hydrocarbons and pesticides by fish in lentic and lotic ecosystems. pp. 262-281. In: *Fate of Pollutants in the Air and Water Environments - Part 2. Chemical and Biological Fate of Pollutants in the Environment*. Vol. 8. I.H. Suffet (ed.).

Hanners, L. 1968. Experimental investigations on the accumulation of mercury in the water organisms. Inst. Freshwater Res. Drottningholm 48: 120-176.

Harvey, H.H. 1975. Fish populations in a large group of acid-stressed lakes. Verh. Internat. Verein. Limnol. 19:2406-2417.

Harvey, H.H. Personal communication. University of Toronto, Toronto, Ontario.

Hodson, P.V. and E.S. Millard. 1977. Experimental ecosystems as a means of evaluating the fate and effect of contaminants in aquatic ecosystems. In: Proceedings of the 4th Annual Toxicity Workshop, Vancouver, B.C., November 1977. Fish. Mar. Serv. Tech. Report.

Huckabee, J.W., R.A. Goldstein, S.A. Janzen and S.E. Wock. 1975. Methylmercury in a freshwater food chain. p.199-215. International Conferences on Heavy Metals in the Environment Symposium Proceedings Vol. II, Part I, October 27-31, 1975. Toronto, Ontario, Canada.

Humason, G. 1972. Animal Tissue Techniques. W.H. Freeman and Company, San Francisco. 641 pp.

Jernelov, A. and H. Lann. 1971. Mercury accumulation in food chains. Oikos 22:403-406.

Johansson, N., J.E. Kihlstrom and A. Walberg. 1973. Low pH values shown to affect developing fish eggs (Brachydavine cecis, Hasn-Buch). Ambio 2:1-2.

Knoechel, R. and J. Kalff. 1976a. The applicability of grain density autoradiography to the quantitative determination of algal species production: A critique. Limnol. Oceanogr. 21(4):583-590.

Knoechel, R. and J. Kalff. 1976b. Track autoradiography: A method for the determination of phytoplankton species productivity. Limnol. Oceanogr. 21(4): 590-596.

Krenkel, P.A. 1974. Mercury: environmental considerations. Part II. Chemical Rubber Co. Crit. Review Environ. Control 4(3): 251-339.

Kwiatkowski, R.E. and J.C. Roff. 1976. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. Can. J. Botany 54(22): 2546-2561.

Landner, L. and P.O. Larsson. 1972. IVL Report B115-Swedish Institute for Water and Air Pollution Research, Stockholm. (In Swedish).

Leivestad, H. and I.P. Muniz. 1976. Fish kill at low pH in a Norwegian River. Nature 259:391-392.

Leivestad, H., G. Hendrey, I.P. Muniz and E. Snekvik. 1976. Effects of acid precipitation on freshwater organisms. pp.87-111. In: F.H. Braekke (ed.). Impact of acid precipitation on forest and freshwater ecosystems in Norway. Research Report 6. Agricultural Research Council of Norway, Norwegian Council for Scientific and Industrial Research.

Likens, G.E., R.F. Wright, J.N. Galloway and T.J. Butler. 1979. Acid rain. *Scientific American* 241(4): 43-52.

Lloyd, E.T., W.T. Schnemk and J.O. Stoffer. 1977. Mercury accumulation in trout of southern Missouri. *Environ. Res.* 13:62-73.

Lock, R.A.C. 1975. Uptake of methylmercury by aquatic organisms from water and food. Sublethal effects of toxic chemicals on aquatic animals. *Proc. Swedish-Netherlands Symp.* J.H. Koeman and J.J. T.W.A. Stik (eds.) pp.61-79.

Menendez, R. 1976. Chronic effects of reduced pH on brook trout. *J. Fish. Res. Bd. Canada* 33:118-123.

Miller, D.R. and H. Akagi. 1979. pH affects mercury distribution not methylation. *Ecotoxicology and Environmental Safety* 3:36-38.

Mount, D.I. 1973. Chronic effect of low pH on fathead minnow survival, growth and reproduction. *Water Res.* 7:987-993.

Norstrom, R.J. and M. Brounstein. 1974. Chemical analysis, 1972-1973. Report A, pp.19A1-19A50. In: *Distribution and Transport of Resistant Chemicals in Flowing Water Ecosystems*. D.R. Miller (ed.). Report No. 2, Ottawa River Project. Div. Biol. Sci. Natl. Res. Counc. Car. Ottawa, Ontario.

Norstrom, R.J., A.E. McKinnon and A.S.W. de Freitas. 1976. A bioenergetic model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa yellow perch (Perca flavescens). *J. Fish Res. Bd. Canada* 33(2):248-267.

Phillips, G.R. and D.R. Buhler. 1978. The relative contributions of methylmercury from food or water to rainbow trout (Salmo gairdneri) in a controlled laboratory environment. *Trans. Am. Fish Soc.* 107(6):853-861.

Phillips, G.R. and R.C. Russo. 1978. Metal bioaccumulation in fishes and aquatic invertebrates: A literature review. *EPA-600/3-78-103*.

Rand, M.C., A.E. Greenberg, M.J. Taras and M.A. Franson. 1976. Standard Methods. American Public Health Association, American Water Works Association, Water Pollution Control Federation. 1193 pp.

Reeder, S.W., A. Demayo and M.C. Taylor. 1979. Mercury. In: *Guidelines for Surface Water Quality*. Vol. I. Inorganic Chemical Substances. Environment Canada. Inland Waters Directorate, Water Quality Branch. 16pp.

Rodgers, D. Personal Communication. University of Guelph, Guelph, Ontario.

Roff, J.C. and R.E. Kwiatkowski. 1977. Zooplankton and zoobenthos communities of selected northern Ontario lakes of different acidities. *Can. J. Zool.* 55:899-911.

Rogers, A.W. 1973. Techniques of Autoradiography. Elsevier, Amsterdam, London, New York. 372p.

Ryan, P.M. and H.H. Harvey. 1979. Growth responses of yellow perch, Perca flavescens (Mitchell), to lake acidification in the La Cloche Mountain Lakes of Ontario. Unpublished manuscript.

Salazkin, A.A. 1971. Zooplankton in oligotrophic lakes of the humid zone in the northwestern USSR. Gibrobiol. Zh. 7:23-28.

Scheider, W., I. Adamski and M. Paylor. 1975. Reclamation of acidified lakes near Sudbury, Ontario. Ontario Ministry of the Environment. 129 p.

Schindler, D.W. 1979. Acid rain. A lecture presented at British Columbia Hydro and Power Authority, Vancouver, B.C. November 13, 1979.

Schofield, C.L. 1976. Effects of acid precipitation on fish. Presented at International Conference on the Effects of the Acid Precipitation. Telemark, Norway. June 14-19, 1976. 20pp.

Sprague, J.B. 1973. The ABC's of pollutant bioassay using fish, pp. 6-30. In: Biological Methods for the Assessment of Water Quality. ASTM, STP 528. American Society for Testing and Materials. 256 pp.

Sprules, W.G. 1975. Midsummer crustacean zooplankton communities in acid-stressed lakes. J. Fish. Res. Bd. Canada 32:389-395.

Suns, K. 1978. Personal communication. Limnology and Toxicity Section. Ministry of the Environment, Ontario.

Suns, K., C. Curry and D. Russell. 1980. The effect of water quality and morphometric parameters on mercury uptake by yearling yellow perch (Perca flavescens). Technical Report L.T.S. 80-1.

Tsai, S.C., G.M. Boush and F. Matsumura. 1975. Importance of water pH in accumulation of inorganic mercury in fish. Bull. Env. Contam. Toxicol. 13(2): 188-193.

Yan, N.D. W.A. Schneider and P.J. Dillon. 1977. Chemical and biological changes in Nelson Lake, Ontario following experimental elevation of lake pH. Proc. 12th Canadian Symposium 1977: Water Pollution Research Canada.

ATMOSPHERIC DEPOSITION OF MERCURY IN ONTARIO

BY

S.C. BARTON, N.D. JOHNSON AND J. CHRISTISON

ONTARIO RESEARCH FOUNDATION

SHERIDAN PARK RESEARCH COMMUNITY

MISSISSAUGA, ONTARIO

AND

S. GEWURTZ*

ONTARIO MINISTRY OF THE ENVIRONMENT

880 BAY STREET

TORONTO, ONTARIO

PRESENTED AT

ONTARIO MINISTRY OF THE ENVIRONMENT

TECHNOLOGY TRANSFER CONFERENCE NO. 1

SKYLINE HOTEL

NOVEMBER 25, 1980

* Present Affiliation: Ministry of Labour
400 University Avenue
Toronto, Ontario

ABSTRACT

The cause of elevated mercury levels in fish of freshwater lakes remote from known sources in Ontario and elsewhere has yet to be identified. The importance of atmospheric transport of mercury from remote sources to land and water surfaces in Ontario has been investigated in this study. Improved sampling and analytical methodology for the measurement of mercury in air and precipitation have been developed and a field study was conducted for six months which included both a suburban and remote site. Continuous and cumulative sampling techniques were used simultaneously to measure airborne mercury levels and the relative importance of elemental, organic and particulate components was assessed. Conventional wet deposition sampling techniques were modified to enable proper compensation for mercury vapour uptake by preservative solutions. Prevailing ambient concentrations were generally consistent with earlier studies (1 to 10 $\text{ng} \cdot \text{m}^{-3}$) with elemental mercury being the main constituent. Particulate mercury accounted for less than 15% of the total mercury and organomercury vapour was essentially non-detectable. Directional patterns showed little evidence of a predominant long range transport mechanism for airborne mercury. Wet deposition was found to make a considerably more important contribution (~ 20 to $30 \text{ } \mu\text{g} \cdot \text{m}^{-2} \text{ year}^{-1}$) than dry particulate deposition whereas preliminary vertical profile measurements indicated that dry vapour deposition may be of major importance. Based on the experimental results, the total flux of mercury to the land surface in Ontario is in the range of 75 to $140 \text{ } \mu\text{g} \cdot \text{m}^{-2} \text{ year}^{-1}$ and thus similar to continental deposition rates assumed in recent global mercury budgets.

INTRODUCTION

The occurrence of elevated mercury levels in fish of freshwater lakes remote from known sources in Ontario, and elsewhere, is still not fully understood. The objective of this study was to obtain experimental data which would help to define the possible role of the atmosphere as a medium for the transfer of mercury to land and water surfaces remote from known sources.

Environmental concern about mercury appears to have commenced as early as 1700 when a citizen of an Italian town sought an injunction against a factory making mercuric chloride because it's fumes apparently were killing people in the town. However, current environmental concern about mercury is based largely on experiences of the past two decades, and has arisen primarily from the acute toxic effects which have occurred amongst people eating fish and seed grain contaminated with mercury compounds (1). Much has been written on these incidents and, in Canada, the subject has received attention since the late 1960's when rivers and lakes in Ontario were closed to fishing because of mercury pollution. In the early incidences contamination could generally be traced to some local industrial source, but as the investigations continued, mercury was found to exist in numerous organisms and the environment in general, with significant amounts being found in areas quite remote from any known sources. Rivers in Northern Ontario, and lakes in the Muskoka district of Ontario, the Adirondacks in New York State and Southern New Brunswick were specific areas of concern.

Natural processes which have been releasing mercury to the environment for billions of years include the weathering of mercury-containing mineral formations, soil degassing and volcanic emanations, and to a lesser extent, emissions from land biota (Table 1). Major anthropogenic sources from which mercury can be emitted into the atmosphere include the combustion of fossil fuels, sulphide ore smelting, cement production, the Chlor-Alkali process, incineration and numerous other uses. As a result of these many and diverse uses, in conjunction with the numerous natural sources, mercury is an ubiquitous element found throughout the environment in its various chemical forms.

Global mercury cycles have been derived in recent years in an attempt to provide at least a semi-quantitative assessment of the relative importance of

natural and anthropogenic sources and to define the relative importance of the various pathways and sinks (2, 3). It is now generally accepted that the atmosphere can be an important transport medium for mercury, with a currently estimated residence time of only 11 days, compared to thousands of years for other compartments of the environment. However, relatively little direct experimental evidence is available regarding the transport and deposition mechanisms whereby mercury is removed from the atmosphere and transferred to land and water surfaces.

OBJECTIVES OF STUDY

The attainment of a better understanding of the atmospheric transport and subsequent deposition of mercury on land and water surfaces in Ontario was the overall objective of this study. Specific objectives were:

- to collect experimental data on the atmospheric levels and deposition rates of mercury
- to define deposition flux to land and water surfaces in specific urban and rural areas of Ontario
- to characterize predominant transport and deposition mechanisms and species

Specific phases of the study were:

- literature review to collect all relevant information
- development of sampling and analytical methodology to quantitatively define both airborne concentrations and deposition rates of particulate and vapour mercury
- assembly of a field monitoring facility
- six-month field survey at two sites
- assessment of the experimental data.

The ubiquitous occurrence of low levels of mercury throughout the environment provides a special challenge in attempting to quantitate atmospheric levels. The development and evaluation of appropriate methods, both sampling and analytical, was an essential and important component of the study, and the

details of this phase of the work are described elsewhere (4).

EXPERIMENTAL METHODS

Field studies were initiated in February 1979 in Sheridan Park, and continued in the Dorset area until mid-August. The studies at Sheridan Park were designed primarily to field test the equipment and methods but also to provide information on mercury levels and characteristics in an urban area. The Dorset site was selected as being representative of the Muskoka area. The monitoring and sample collection activities undertaken can be summarized as follows:

- measurement of atmospheric levels of elemental, particulate and organic mercury, with both continuous and cumulative measuring techniques
- measurement of mercury content of both wet and dry deposition samples on both a "routine" and "event" basis
- measurement of dry vapour deposition by velocity profile measurements
- measurement of meteorological parameters such as wind direction and speed, rainfall, humidity, temperature and pressure.

The field equipment used to achieve these measurements is shown schematically on Figure 1 and consisted of:

- Scintrex continuous mercury monitor
- cumulative 24-hour sampling train capable of differentiating between particulate, elemental and organomercury compounds, based upon amalgamation of mercury with silver. Organomercury compounds pyrolyzed prior to collection on one side of parallel collectors
- calibration equipment for static mercury vapour injection
- high-volume sampler
- cascade impactor used occasionally on high-volume sampler
- automatic wet/dry deposition sampler and conventional bulk sampler
- meteorological equipment including wind direction and speed, barograph, hygrothermograph and rain/snow gauge.

The system was designed for unattended operation for periods of several days. Wet, dry and total deposition samples were collected in nitric acid/potassium dichromate preservative solutions (5) and extensive blank procedures were instituted to make allowance for the uptake of mercury vapour by the acidic solutions and for other possible sources of contamination. Precipitation samples were collected on both a weekly and event basis.

All samples were analyzed by cold vapour atomic absorption spectrophotometry after appropriate sample extraction and digestion procedures.

DISCUSSION OF RESULTS

Predominant Species

Mercury emissions from anthropogenic sources are known to be predominantly in the elemental form, whereas natural sources involving biological processes are believed to give rise to organomercury compounds. The principal classes of mercury generally considered to occur in the atmosphere are (6):

- elemental mercury vapour
- mercury chloride vapour and other volatile salts
- various species adsorbed on particulate matter
- organomercury compounds such as methyl and dimethylmercury.

The monitoring techniques utilized in this study were designed to quantitatively define the relative importance of elemental mercury vapour, total organomercury (vapour) compounds, and total particulate mercury. The overall results indicate the following proportions of elemental, organic and particulate mercury:

<u>CLASS</u>	<u>% OF TOTAL</u>	
	<u>SUBURBAN</u>	<u>REMOTE</u>
Elemental	84	89
Organic (vapour)	4	3
Total particulate	12	8

Thus, the results quantitatively confirm the predominance of elemental mercury in the atmosphere and the observed percentages of other components also are in general agreement with earlier studies. A statistical evaluation of the data lead to the conclusion that the calculated difference between

"total" and "elemental" measurements (equal to the organomercury compound) was not significant at the 95% confidence level. This, and other features of the data, indicate that organomercury species do not play an important role in atmospheric transport and deposition processes.

Prevailing Ambient Levels and General Features

Airborne mercury concentrations have been reported to depend on the geographical locations, meteorological conditions, altitude, season of the year and time of day. Unfortunately, conflicting reports exist in many instances. The range of mercury concentrations usually cited for unpolluted air is $1-10 \text{ ng.m}^{-3}$, whereas levels from less than 1 ng.m^{-3} in remote areas to tens of thousands of ng.m^{-3} near point sources are reported (7). The levels measured in this study are summarized in Table 2. The predominance of elemental mercury is apparent and the levels at the remote site were consistently lower than in the urban area. At Dorset, all hourly values were below 20 ng.m^{-3} , whereas a considerably larger range (up to $\sim 200 \text{ ng.m}^{-3}$) was observed at the urban site. The measured 24-hour levels are in good agreement with the results of earlier studies which are summarized in Table 3 (8).

The potential influence of meteorological parameters on mercury levels has been discussed in the literature. Inspection of the data (primarily in the form of diurnal profiles) showed no apparent correlation at either site of ambient mercury levels with parameters such as temperature, relative humidity, barometric pressure or wind speed. However, correlation of elemental mercury levels with wind direction showed patterns of considerable interest, as shown in Figure 2. At Sheridan Park, higher than average mercury concentrations correlated quite strongly with Easterly winds. Specific features of the results that indicate the higher mercury concentrations from Easterly Directions were the result of local point sources rather than long-range transport are:

- fairly abrupt changes in mercury concentration-time profiles in conjunction with wind shifts, and
- rapidly fluctuating mercury levels (five-fold increases typically occurred within a few minutes) rather than high continuous levels during the events.

The observed high levels from NE - E directions could be the results of emissions from several sources:

- Sheridan Park laboratory and Pilot Plant facilities (to the ENE - E)
- The Lakeview generating station (to the ENE)
- The Toronto/Mississauga urban plume (N - NE sector).

The highly structured concentration-time profiles and, to a lesser extent, the relatively low levels from N and NNE directions indicate that a diffuse urban plume was not the predominant source of mercury at this site. The highest levels from easterly directions are consistent with the presence of the very local potential sources mentioned above. The NE contribution could be attributed to either local emissions or the Lakeview generating station.

Wind frequency distributions for the survey period are also shown in Figure 2 and must be taken into account in assessing directional distributions expressed as average concentrations. Directional distributions of total dosages (concentration X time) for each wind direction were also calculated. This directional profile is considerably different from that based upon average concentrations, and the relative magnitudes for each direction are very similar to the wind frequency pattern. Thus, despite the observation of occasional periods of relatively high mercury levels associated with winds from the direction of potential sources, it must be concluded that there is really no predominant source contributing to average mercury levels at this suburban location.

The Dorset data are presented in a similar fashion in Figure 3. Consistently low mercury levels in this area (overall mean concentration $\approx 3 \text{ ng.m}^{-3}$) were determined by both sampling techniques. As already discussed, the minimal daily variation about the mean and lack of events were other important features of the data. No significant directional distribution of average concentrations was found for either the hourly or daily measurements. As shown by the wind frequency distribution, winds from the SE quadrant occurred only a small portion of the time and thus measurements under these conditions were very infrequent. A directional distribution of mercury dosage also was calculated for the Dorset site and is virtually identical to the wind frequency distribution. This, and other features of the data, demonstrates the lack of any specific, predominant long-range transport mechanism which contributes to ambient mercury levels in the Dorset area.

Deposition Measurements

Concern with the fate of atmospheric pollutants and their potential impact on the aquatic and terrestrial environment has resulted in an increased interest in removal processes in recent years. An important component of this study has been the experimental determination of the mercury flux to land and water surfaces which can be expected to occur in Ontario.

Atmospheric deposition processes whereby pollutants can be removed from the atmosphere are many and complex, but can be arbitrarily divided into two categories, wet and dry, and each category can in turn be subdivided with respect to the removal of gases and particulates. Wet processes include rainout from clouds, washout under clouds and chemical transformations between aerosols and water droplets.

Dry deposition is the direct transfer of material from the atmosphere to the earth's surface. Processes affecting dry deposition of a pollutant include gravitational settling, transport by atmospheric turbulence, impaction, heterogeneous and homogeneous reactions, concurrent surface fluxes, and adsorption and absorption processes of both atmospheric aerosols and various constituents on the receptor surface. Simple conceptual definitions of the wet and dry deposition processes have been used to evaluate the experimental results obtained in this study (9).

Total, wet and dry particulate deposition samples were collected on both a weekly and event basis, using preservative solution to trap and stabilize the mercury constituents. Blanks were exposed to compensate for vapour uptake by the solution. An automated Sangamo sampler was used to collect wet samples. An attempt was also made to measure directly dry deposition, using the other side of the sampler, and a "bulk" or total deposition was also collected in an open beaker. After defining methods and conducting limited studies at Sheridan Park, a total of ~ 11 weekly samples and 8 events were collected at the Dorset site. The mean wet deposition rate was $0.4 \mu\text{g.m}^{-2} \text{wk}^{-1}$ (or event) with individual values ranging from ND to $0.8 \mu\text{g.m}^{-2} \text{wk}^{-1}$. The average mercury concentration in precipitation was 0.02 ppb. The results are summarized in Table 4 in terms of annual loadings.

Important features of the wet deposition results are:

- only minor variations occurred in mercury concentrations, and so variations in deposition flux depended primarily on quantity of precipitation
- slightly higher concentrations were usually obtained in event than in weekly sampling, but this may be due to a larger particulate contribution to the event samples
- average amounts of rainfall fell during the survey period on both a seasonal and yearly basis
- The results are in good agreement with earlier precipitation (snow) studies conducted in Quebec and Ontario (10).

Considerable disagreement exists as to the efficiency of precipitation in washing out relatively insoluble mercury vapours (11, 12). The continuous mercury measurements made during rainstorms permitted a direct assessment of this effect. The concentration profiles during precipitation events did not show clear evidence of an effective washout mechanism which either increased or reduced mercury levels. In any event, both washout coefficient and scavenging ratio calculations (9) were made for comparison with the experimental results. The scavenging ratio results, shown in Table 4 gave the better agreement with the experimental results.

The directly measured dry particulate deposition component of the total mercury flux was non-detectable at Dorset (Table 4). The somewhat higher contribution determined from the difference between the total and wet collections is believed to be less accurate than the direct measurements because of inadequacies in the blank corrections that were available for this sampling mode. The calculated dry deposition flux values were determined using mass median particulate diameters measured at the Dorset site by cascade impaction methods. The average measured particulate mercury concentrations, and corresponding deposition velocities of 0.25 and 0.07 cm.sec^{-1} for grass (Dorset) and a smooth surface (snow, Sheridan Park)(9), respectively. The calculated values are higher than, but of the same magnitude as, the measured rates, confirming their basic validity.

As discussed above, the direct absorption of a gas at a surface can be an important mechanism for the removal of pollutants from the atmosphere. Dry vapour deposition velocities for mercury have not been measured experimentally to any significant extent. Estimates in the range of 0.1 to 1.0 cm.sec^{-1} have been made and a value of 0.3 cm.sec^{-1} has been advocated as a suitable estimate for general use (13). For comparison, a typical value for SO_2 is 1 cm.sec^{-1} .

Vertical profile measurements of pollutant concentrations and relevant meteorological parameters can be used to estimate the dry vapour flux occurring under a given set of conditions (14). A limited number of such measurements were made at the Dorset site and the concentration and wind profiles are shown in Figure 4. The lowest sampling point was just above the canopy of tall grass and weeds in the vicinity of the site. Several features of the data can be noted:

- an unexpected minimum in the mercury concentration profile appears to occur at $\approx 1.4 \text{ m}$ with the effect being more predominant under daytime conditions. If this minimum is ignored and treated simply as scatter in the data, a slight increase in concentration with height is observed, suggesting a relatively small net transfer to the surface
- The fetch of uniform surface upward of the site was at least 100 times the sampling height
- wind speed profiles show an essentially exponential increase with height
- neutral to moderately unstable conditions prevailed during the study period
- ambient mercury levels were quite constant during the study period.

The mean mercury and wind profiles have been used in conjunction with the mass transfer coefficient approach (14) to estimate a deposition flux as follows:

$$F = C_p \cdot U_z (X_z - X_o)$$

where $C_p = 1.35 \times 10^{-3}$

and z , the reference height, was taken to be 10 m.

The day and night profiles were then used to determine the following deposition velocity and flux ranges:

$$V_g = 0.06 \text{ to } 0.1 \text{ cm.sec}^{-1}$$

$$\text{Flux} = 45 \text{ to } 110 \text{ } \mu\text{g.m}^{-2} \text{ year}^{-1}$$

These estimates are slightly lower than the deposition velocities that have been previously assumed. However, the values are very similar to those that can be derived from Hogstrom's (15) recent study of mercury levels and deposition rates near a point source which is the most quantitative and recent assessment of mercury transport and deposition currently available. On the basis of these results and the estimates made using Hogstrom's modelling work, it is concluded that the dry vapour mercury deposition velocity is somewhat lower than previously assumed, and a range of $0.06 - 0.1 \text{ cm.sec}^{-1}$ seems probable at this time. This range, in conjunction with prevailing ambient concentrations at the Dorset site, indicates a dry vapour deposition flux of approximately $45 \text{ to } 110 \text{ } \mu\text{g.m}^{-2} \text{ year}^{-1}$, and consequently it is the most significant component of the total deposition flux.

SUMMARY AND CONCLUSIONS

The results have been used to quantify the major features of a simple model for the atmospheric transport and deposition of mercury (Figure 5) and the results can be summarized as follows:

- Ambient levels of $\approx 10 \text{ ng.m}^{-3}$ total mercury were found in Mississauga, in comparison with $\approx 3.5 \text{ ng.m}^{-3}$ in the Dorset area. The higher levels in Sheridan Park are attributable to specific anthropogenic emissions.
- Elemental mercury vapour was the major component in each area, organomercury vapour was not a significant fraction, and particulate mercury levels were less than 15% of the total mercury. Greater than 50% of particulate mercury occurred in the fine particulate fractions ($< 2.2 \mu\text{m}$). These results are in good agreement with average concentrations reported in other studies for similar urban and remote areas in North America.
- No strong diurnal variation in mercury concentrations was observed at either station and there was no apparent correlation with meteorological parameters (i.e. temperature, barometric pressure, relative humidity and wind speed), which were measured concurrently. Unlike mercury, these parameters in most cases showed quite distinct and consistent diurnal variations.
- Correlations of mercury concentrations with wind direction indicated a local source or sources of predominantly elemental mercury vapour East to Northeast of the Sheridan Park sampling station, consistent with known potential sources. Apart from the few higher levels obtained from the Easterly direction, the mercury input to the area was practically independent of wind direction and was proportional to the wind frequency distribution. The same conclusion holds true for the results at Dorset where low levels ($2-6 \text{ ng.m}^{-3}$) occurred with winds from any direction. Thus, no marked influence of long-range transport from any predominant area or point source is evident at either sampling station.
- A mean wet deposition flux value of approximately $20 - 30 \text{ } \mu\text{g.m}^{-2} \text{ year}^{-1}$ occurred at both sampling areas, although slightly higher mercury concentration in precipitation were found at Sheridan Park in comparison with the values at Dorset, 0.02 and 0.04 ppb, respectively.

- Dry particulate deposition accounted for a relatively minor proportion of the total deposition flux at the suburban station where the directly measured annual flux was found to be $\approx 5 \text{ } \mu\text{g.m}^{-2} \text{ year}^{-1}$. At Dorset the contribution by dry particulate deposition was essentially non-detectable.
- On the basis of limited vertical profile measurements, net dry vapour deposition was estimated to be approximately 45 to 110 $\mu\text{g.m}^{-2} \text{ year}^{-1}$ at Dorset and is thus a major fraction of the total deposition flux. Although this is the least well quantified aspect of the total deposition flux, the estimated dry vapour deposition velocities ($0.06 - 0.1 \text{ cm.sec}^{-1}$), compare favourably with the value of 0.08 cm.sec^{-1} estimated from the results of a recent study near a point source.
- The total deposition flux to land and water surfaces in Ontario was estimated to be 75 to 140 $\mu\text{g.m}^{-2} \text{ year}^{-1}$ and dry vapour deposition, which appears to be the most important component, is least well-defined.

In conclusion, elemental mercury vapour is the predominant atmospheric constituent, and levels found in Ontario are consistent with the results of studies in other areas. Directional patterns and other features of the data show little evidence of a predominant long-range transport mechanism. The estimated total deposition flux in Ontario appears to be similar to continental deposition rates postulated in recent global mercury budgets. The consolidation and integration of the results of this study with those of other on-going aquatic and terrestrial effects studies should be pursued in order to provide a thorough understanding of the mobilization of mercury in the environment.

REFERENCES

1. L.J. Goldwater, Mercury in the Environment, *Scientific American* 224 (5), 1971.
2. National Academy of Sciences, *An Assessment of Mercury in the Environment*, Washington, D.C., 1978 .
3. E.L. Kothny, The Three-Phase Equilibrium of Mercury in Nature, Trace Elements in the Environment, *Advances in Chemistry Series No. 123*, American Chemical Society, 1973.
4. S.C. Barton, N.D. Johnson and J. Christison, *A Study of Atmospheric Mercury Deposition in Ontario*, ORF Report P-2699/G-04 to the Ontario Ministry of the Environment, January, 1980.
5. Environment Canada, *Atmospheric Mercury Deposition Workshop*, Canada Centre for Inland Waters, Burlington, Ontario, May 1979.
6. Battelle Columbus Laboratories, *Multimedia Levels - Mercury*, Report prepared for the U.S. Environmental Protection Agency, NTIS PB 273 201, September 1977.
7. I.G. Sherbin, *Mercury in the Canadian Environment*, Volumes I and II, Report prepared by the Environmental Protection Service, Fisheries and Environment Canada, EPS 3- EC-79-6, April 1979.
8. W.H. Van Horn, *Materials Balance and Technology Assessment of Mercury and its Compounds on National and Regional Basis*, U.S. Environmental Protection Agency, NTIS PB 247 000, 1975.
9. P.J. Denison, J.A. McMahon and J.R. Kramer, *Literature Review on Pollution Deposition Processes*, Project ME 3-6 for Alberta Oil Sands, Environmental Research Program and Syncrude Canada Limited, February 1979.
10. R.J.P. Brouzes, M.O. Farkas, R.A.N. McLean, S.R. McGraw, and G.H. Tomlinson, *Measurement and Effects of Atmospheric Input of Mercury to Lakes*, Paper presented before the Division of Environmental Chemistry, American Chemical Society, Washington, September 1979.
11. H.B. Cooper Jr., G.D. Rawlings and R.S. Foote, *Measurement of Mercury Vapour Concentrations in Urban Atmospheres*, *Instrumental Society of America Trans.* 13 (4), 1974.

12. D.J. Johnson and R.S. Braman, Distribution of Atmospheric Mercury Species Near Ground, *Environmental Science and Technology* 8, 1975.
13. P.J. Barry, An Introduction to the Exposure Commitment Concept with Reference to Environmental Mercury, *Monitoring and Assessment Research Centre Technical Report No. 12*, 1979.
14. Bunsel Environmental Consultants, Particulate and Gaseous Dry Deposition from the Atmosphere to the Earth's Surface, Draft Report for Ontario Ministry of the Environment, August 1978.
15. U. Högström et al, A Study of Atmospheric Mercury Dispersion, *Atmospheric Environment* 13 (4), 1979.

TABLE 1SOURCES OF MERCURYNATURAL

- WEATHERING OF MERCURY-CONTAINING MINERAL FORMATIONS
- SOIL DEGASSING
- OCEANIC EMISSIONS
- VOLCANIC EMISSIONS
- ORGANIC VAPOURS AND PARTICLES FROM LAND BIOTA

ANTHROPOGENIC

- COMBUSTION OF FOSSIL FUELS
- SULPHIDE ORE SMELTING
- CEMENT PRODUCTION
- CHLOR-ALKALI PROCESS
- INCINERATION OF MERCURY-CONTAINING ARTICLES
- NUMEROUS AND VARIED INDUSTRIAL USES INCLUDING -- AGRICULTURE, LABORATORIES, DENTAL, ELECTRICAL APPARATUS, ETC.

TABLE 2

SUMMARY OF MERCURY CONCENTRATIONS

<u>SAMPLE TYPE</u>	<u>AVERAGE DAILY MEANS (ng.m⁻³)</u>	
	<u>SUBURBAN</u>	<u>REMOTE</u>
ELEMENTAL	8.2	3.3
PARTICULATE	1.2	0.3
ORGANIC	~0.4	~0.1
TOTAL	9.7	3.6

TABLE 3

Summary of Current Data on Atmospheric Mercury Levels for
Various Locations

(Van Horn, 1975)

	Range	Mean
	(ng/m ³)	
A. Remote and Rural Areas		
Oceanic		
Particulate	< 0.005-0.06	<0.15
Vapor	0.6-0.7	0.7
Non-mineralized terrestrial		
Particulate	< 0.005-1.9	0.15
Vapor	1-10	4.0
Volcanic		
Particulate + vapor	20-37,000	-
Mineralized terrestrial		
Particulate + vapor	7-20,000	-
B. Urban Areas		
Particulate	< 0.01-220	2.4
Vapor	0.5-50	7.0
C. Industrial *		
Vapor	7-5,000,000	-

*These measurements include chlor-alkali plants, thermometer factories, smelters and mercury mines.

TABLE 4

TOTAL, WET AND DRY PARTICULATE FLUX($\mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$)

	<u>TOTAL</u>	<u>WET</u>		<u>DRY</u>	
		<u>MEAS.</u>	<u>CALC.</u>	<u>BY DIFF.</u>	<u>DIRECT</u>
SHERIDAN PARK	31	23	32	8	5
DORSET	32	21	23	11	ND

Figure 1 - ATMOSPHERIC MERCURY MONITORING UNIT

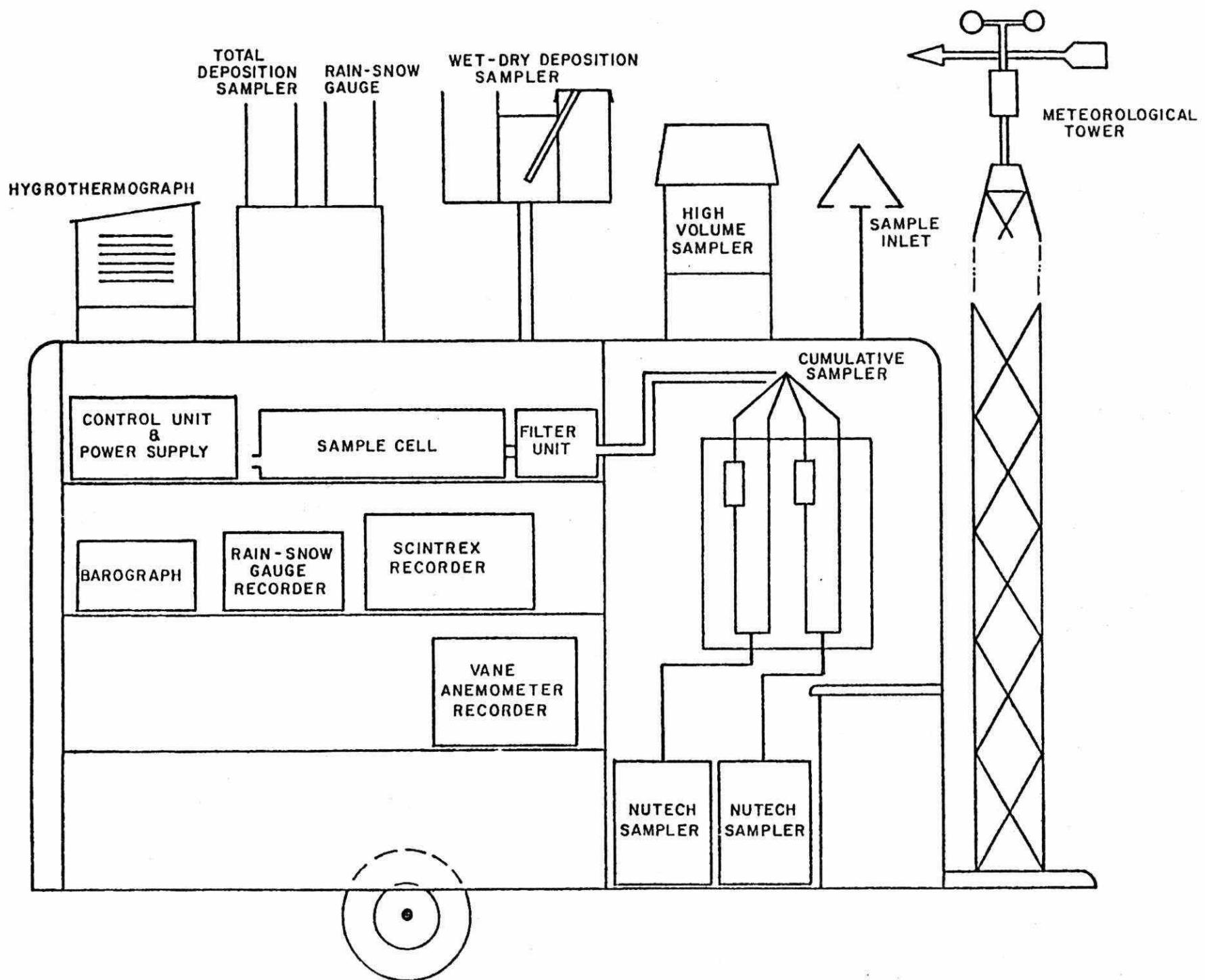


Figure 2 - DIRECTIONAL DISTRIBUTIONS AT SHERIDAN PARK

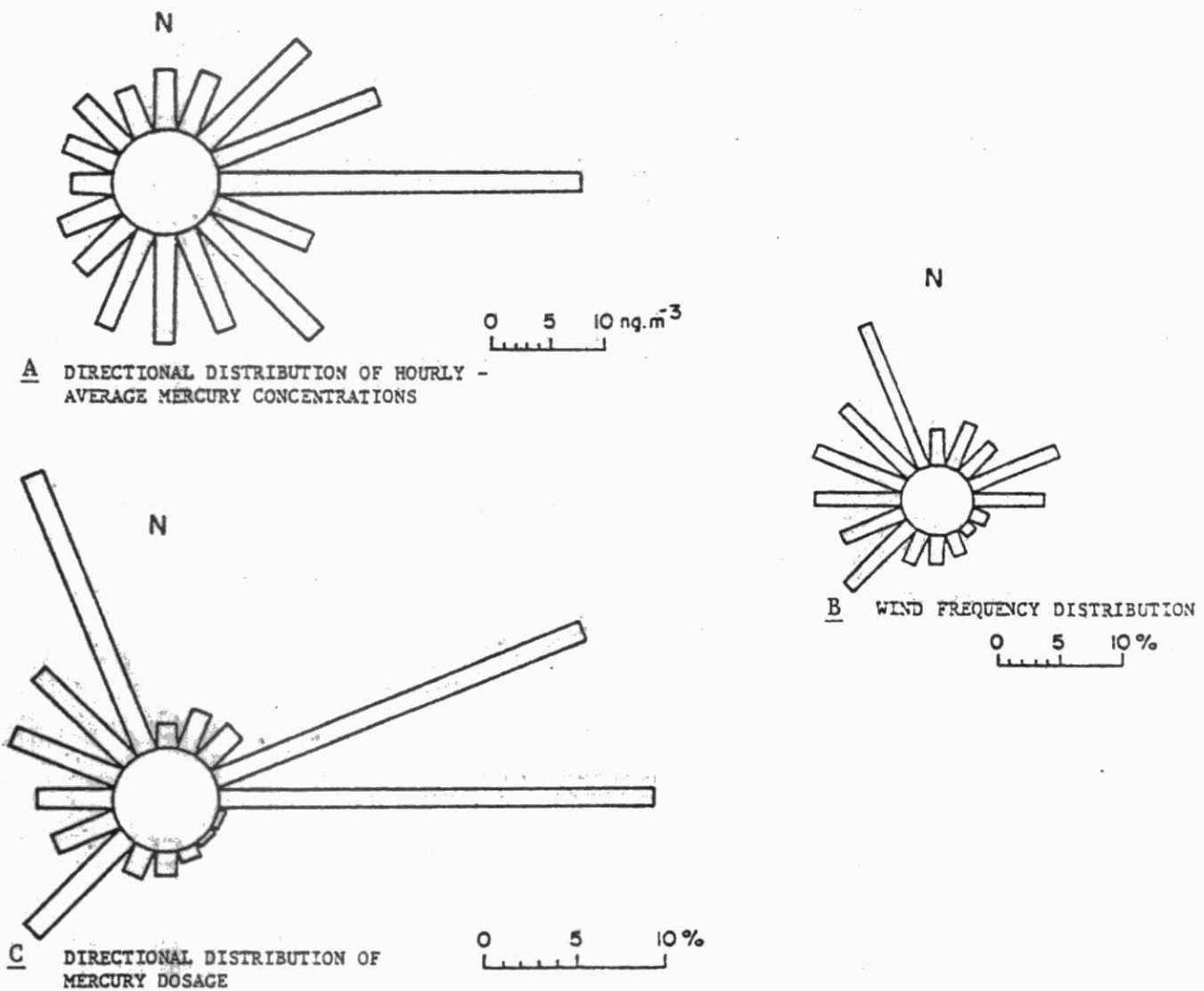
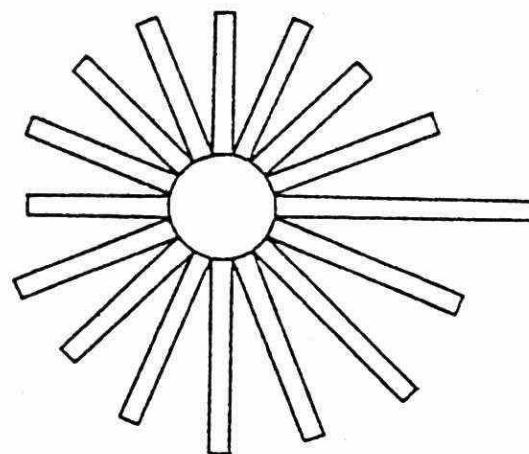
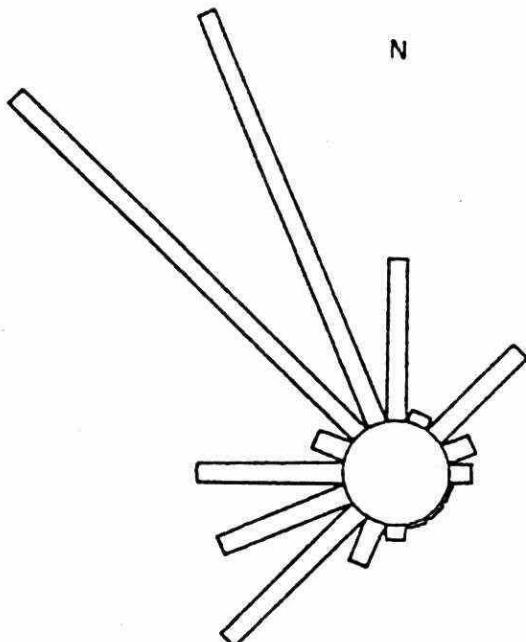


Figure 3 - DIRECTIONAL DISTRIBUTION AT DORSET

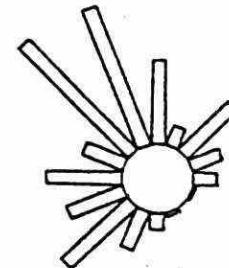
N

0 1 2 $\text{ng} \cdot \text{m}^{-3}$ A DIRECTIONAL DISTRIBUTION OF HOURLY-AVERAGE MERCURY CONCENTRATIONS

N



N



0 5 10 %

B WIND FREQUENCY DISTRIBUTIONC DIRECTIONAL DISTRIBUTION OF MERCURY DOSAGE

Figure 4 - VERTICAL PROFILE SAMPLING AT DORSET
(12-HOUR AVERAGE DETERMINATIONS)

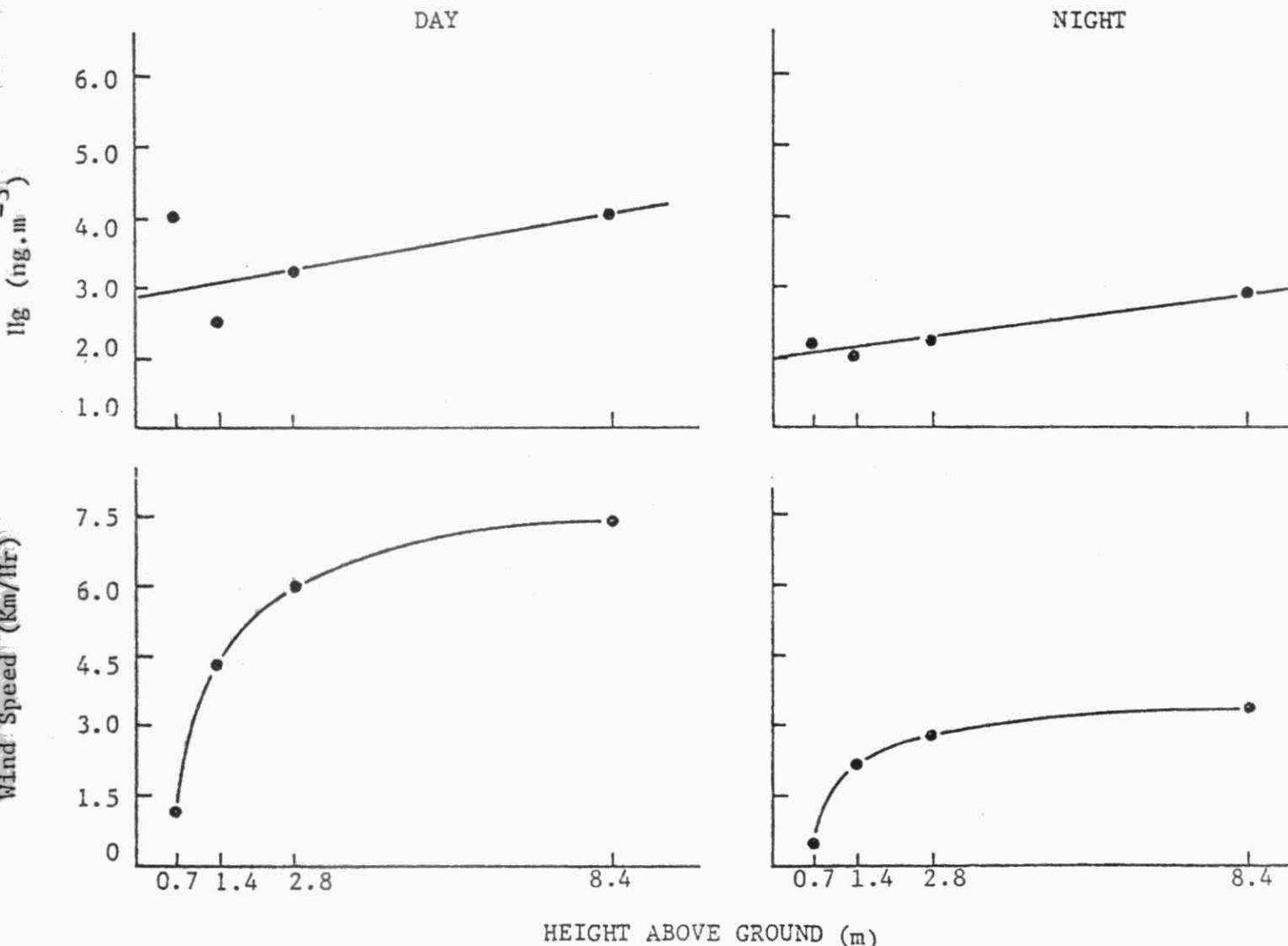
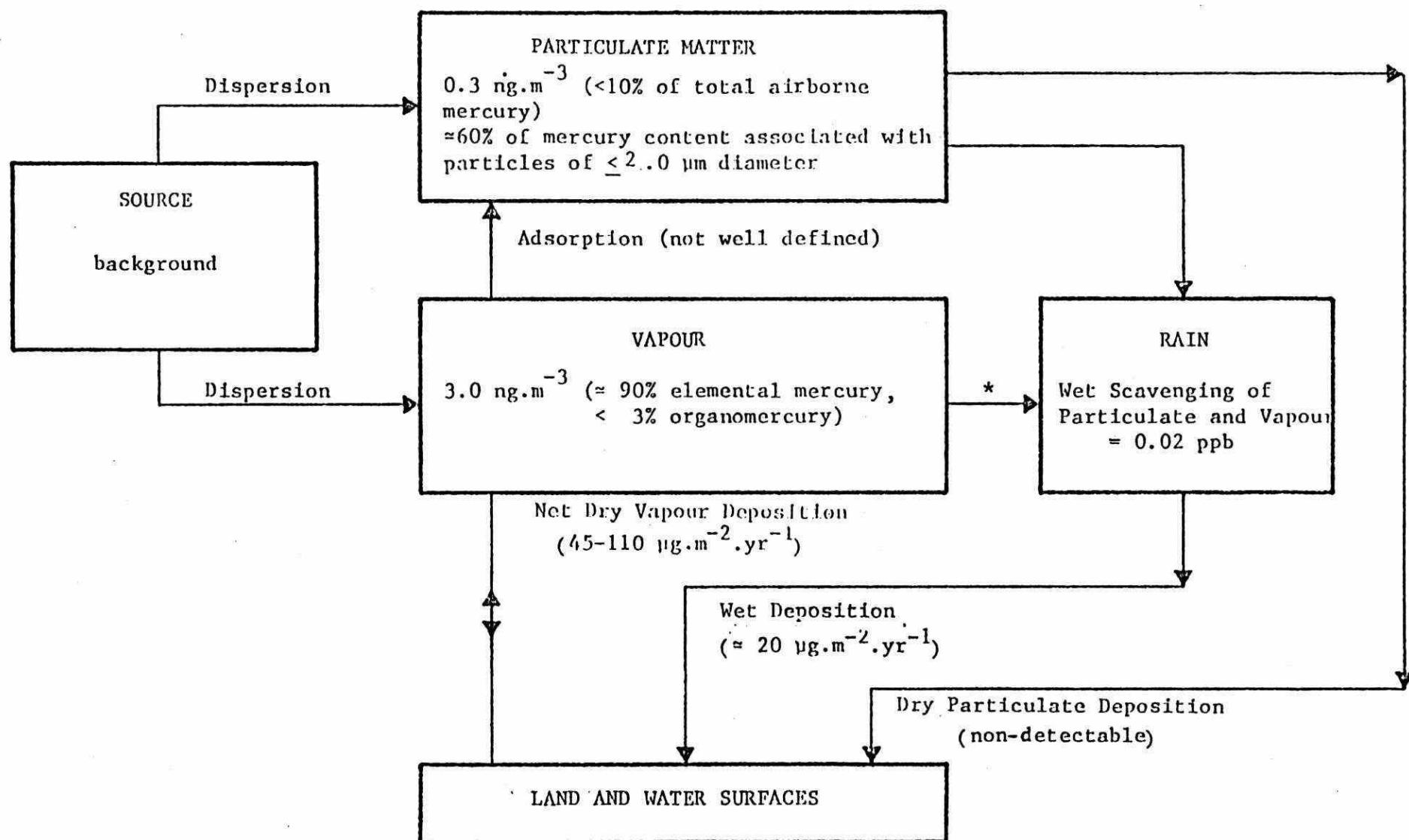


Figure 5 - SUMMARY OF DEPOSITION RATES AND MAJOR PATHWAYS OF AIRBORNE MERCURY TO LAND AND WATER SURFACES IN THE HALIBURTON AREA



* Real-time measurements during precipitation events did not indicate any pronounced washout effect

EVENT PRECIPITATION SAMPLERS
FOR USE IN
ACID RAIN STUDIES

by

D. M. KANE

UNITED TECHNOLOGY and SCIENCE INC.
75 Eglinton Avenue East
Toronto, Ontario M4P 1H3

Presented at the

TECHNOLOGY TRANSFER CONFERENCE NO. 1
Skyline Hotel, Toronto, Ontario
November 28, 1980

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

INTRODUCTION	1
FIELD STUDY	4
RESULTS AND DISCUSSION	8
CONCLUSIONS	17
REFERENCES	18

ACKNOWLEDGEMENTS

I would like to acknowledge the efforts of Dr. Sam Stevens of Concord Scientific Corp., who conceived, designed and assessed the results of the study; Mrs. Margot Brideau for the extensive statistical analysis and Ms. Francis Widmar for the chemical analysis. I would also like to thank the Ontario Ministry of the Environment for sponsoring this study which was financed through the Provincial Lottery Trust Fund.

LIST OF FIGURES

FIGURE 1:	SCHEMATIC DIAGRAM OF WOODBRIDGE AES EXPERIMENTAL STATION	5
FIGURE 2:	SAMPLER ARRANGEMENT	6
FIGURE 3:	TABLE OF BETWEEN SAMPLER VARIATION	9
FIGURE 4:	RATIOS OF H^+ CONCENTRATION	11
FIGURE 5:	RAINFALL RECOVERY RATIOS	11
FIGURE 6:	AEROCHM METRICS SAMPLER CORRELATION COEFFICIENT MATRIX - ALL EVENTS	13
FIGURE 7:	AEROCHM METRICS SAMPLER CORRELATION COEFFICIENT MATRIX - LOW CONTAMINATION INDEX (≤ 11)	15
FIGURE 8:	AEROCHM METRICS SAMPLER CORRELATION COEFFICIENT MATRIX - HIGH CONTAMINATION INDEX (> 11)	16

INTRODUCTION

Up until relatively recently, the sampling of precipitation for chemical analysis was thought to be a fairly simple matter and consequently it was common for fairly simple approaches to be used. These included a variety of designs of open containers, constructed of a number of materials, and these were left out at the sampling sites for varying periods, typically the order of a month. In the early 1970's, a number of investigators became concerned about this type of approach and several studies were conducted (1-5) to compare the performance of different precipitation sampler designs and sampling methodologies. These studies have yielded a number of important conclusions of which the following are relevant to the work described here:

- The ratio of monthly bulk deposition to monthly wet deposition is significantly greater than 1.0 for several parameters
- Results from composite samples for sampling periods greater than one week can be very different from those obtained by summing amounts in individual storm samples over the same periods
- The Hubbard-Brook (funnel and plastic bottle) and the Health and Safety Lab. (HASL) have been found to be the most satisfactory samplers
- All of the automatic samplers perform unsatisfactorily during rain - freezing rain - snow episodes
- The time of storage of samplers should be minimized

- Wind shields do not consistently improve the collection efficiency of a precipitation sampler relative to a standard rain gauge
- Evaporation can be a serious problem
- Automatic samplers have poor snow collection efficiency
- For snow collection, the sampler height to diameter ratio is an important factor in collection efficiency
- Standard rain and snow gauges are necessary to determine the precipitation quantity.

The data available to date indicates that an automatic wet only type sampler operated in an event mode would satisfactorily minimize the dry deposition and other contaminant contributions to a collected rain sample, and thus provide reliable data upon which meaningful interpretations could be made. However, the relatively high cost (2-5K capital, several hundred dollars installation and maintenance costs) makes the use of this type of sampler for an event network of any appreciable size somewhat unattractive financially. Thus, if a satisfactory, inexpensive alternative could be found, it would represent a significant step forward in event precipitation sampling.

Designs which have been used for inexpensive precipitation sampling include the M.O.E. "Sudbury Environmental Study Event" sampler. This is a simple device consisting of a large mouth plastic bucket lined with a polyethylene bag. The polyethylene bag has been modified so as to form a funnel shape at the collection surface thus minimizing contamination. However, because of the wide mouth of the collection, and the fact that it is open for a full 24 hour period with the possibility of dry periods in this interval, the possibility of a sample contamination is greater than for automatic samplers.

Another design that has sometimes been used is the "funnel and bottle" design. This sampler uses a large plastic funnel to collect precipitation which is drained into a bottle. This design affords a relatively large collection area while at the same time offering a relatively small area for dry deposition or other contamination.

To assist in the selection of a satisfactory sampler, a comparative study of the three types of samplers, described above, was carried out for the Ontario Ministry of the Environment. The samplers were operated for 24 hours for each event and the study ran from mid-August to the end of November 1979.

FIELD STUDY

The site for this investigation was the Atmospheric Environment Service's Experimental Station at Woodbridge, Ontario. A rough map showing the study site location is given in Figure 1. This site was well equipped having, in addition to the equipment used for this study, a variety of instruments including: a Fisher-Porter rain gauge; Tipping Bucket Rain gauge; 2 x 10m meteorological towers with anemometers; 2 Sangamo automatic rain samplers, one operated by the M.O.E. and the other by CCIW; 2 CCIW bulk samplers and a M.O.E. storage gauge.

The sampling instruments used in this study were two Aerochem Metrics automatic event samplers, designated as A in the study; two funnel and bottle samplers, designated F; and two Sudbury Environment Study events samplers, designated S. Also, two strip chart recorders installed in a covered box were used to record the open/close cycle of the automatic samplers. The actual sampler arrangement is illustrated in Figure 2.

The sampling procedure is as follows:

At approximately 0830 hours, an assessment by MEP Company meteorologists was made of the probability of precipitation occurring that day. If the probability was greater than 25%, then carefully cleaned (de-ionized H₂O washed) sample containers were transported to the site in clean plastic bags and installed in the samplers. The installation was usually complete by 0930 hours. The samples were picked up at 0930 hours the following day, and, if rain was forecast for that day as well, a new set of containers was installed in the rain samplers. The collected samples were transported immediately to the laboratory and the pH and sample volume were determined

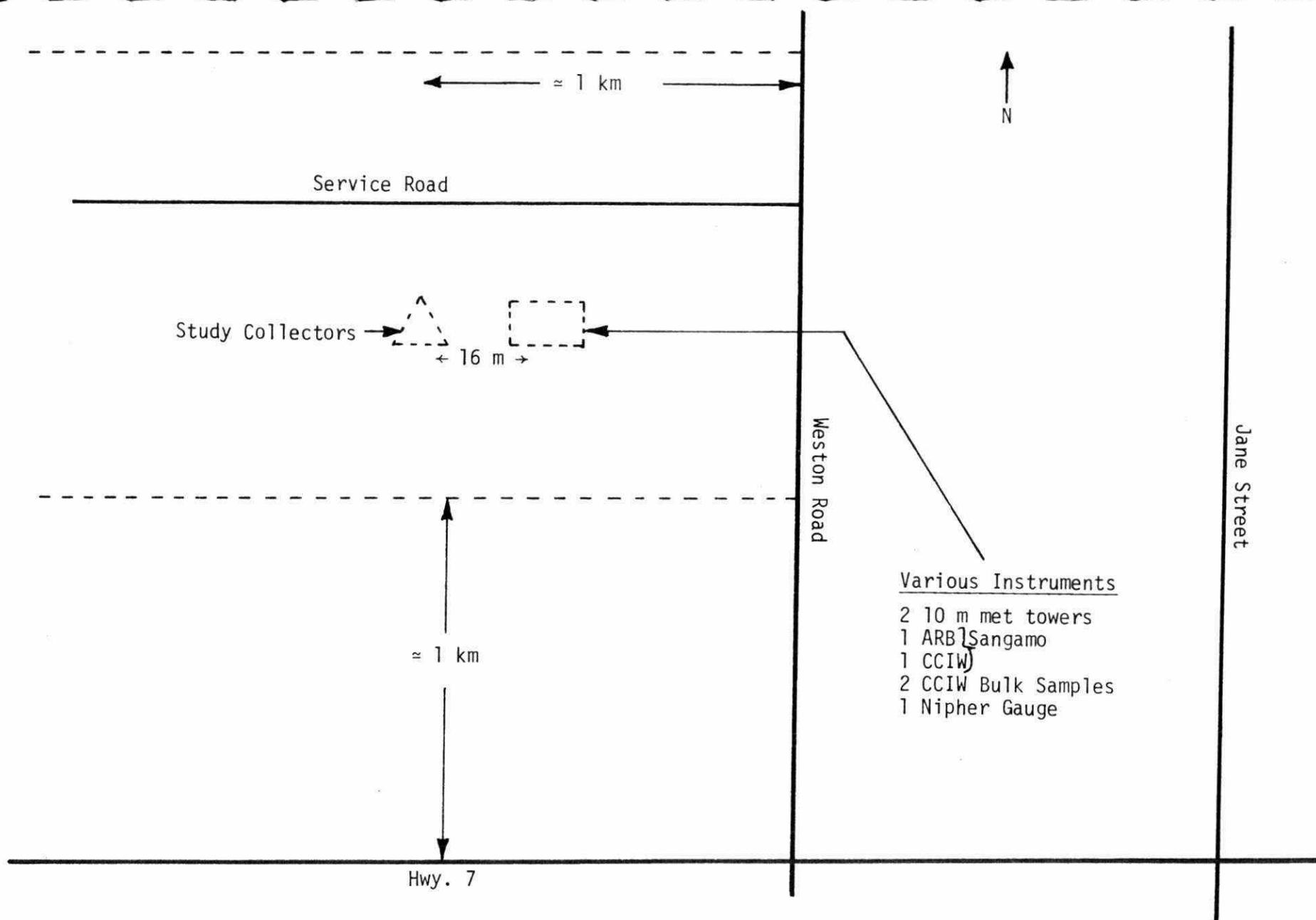
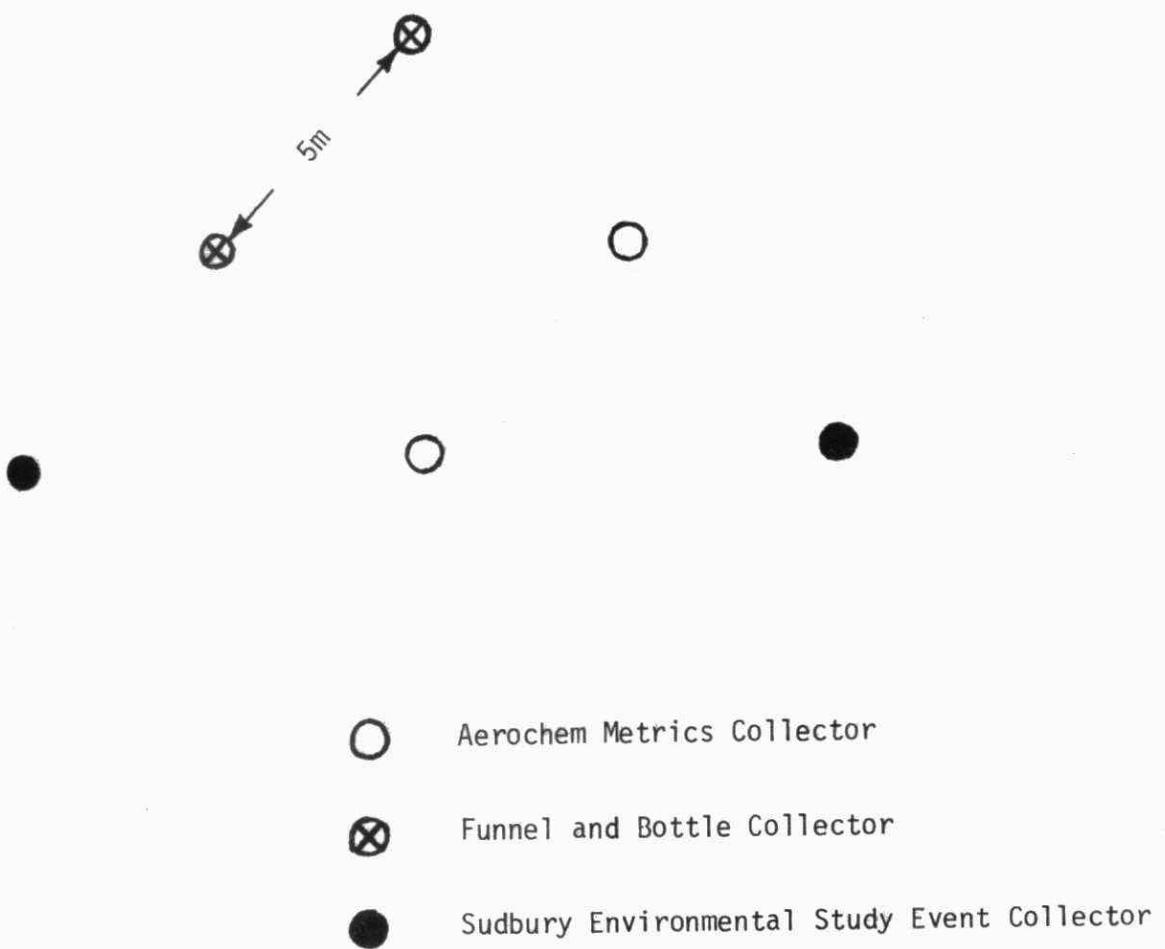


FIGURE 1: SCHEMATIC DIAGRAM OF WOODBRIDGE AES EXPERIMENTAL STATION

FIGURE 2: SAMPLER ARRANGEMENT



as soon as possible (typically $\frac{1}{2}$ hour) after pick-up. The samples were then stored in polyethylene bottles at approximately 4°C until analysis. The storage time before analysis varied from one week to about two months.

Analysis was carried out usually from 1 week to about 2 months after collection. In all, 32 events were sampled over the period of the study.

Analysis of the samples was carried out for pH, sulphate, nitrate, bromide, chloride, fluoride, sulphite, nitrite, phosphate, sodium, potassium, magnesium, calcium and ammonium ions and conductivity. Except for pH and conductivity, all analyses were carried out using ion chromatography. It was found that concentrations of bromide, sulphite, nitrite and phosphate were so low that they were totally masked by the presence of much more dominant ions (e.g. sulphate and nitrate) in the chromatogram, and thus these ions are subsequently not considered.

A laboratory intercomparison study of analytical methods was carried out with the Water Quality Section of the Laboratories Branch of the OME. No significant difference between results from the two labs were found.

RESULTS AND DISCUSSION

The concentration data for each parameter measured over the 32 events of the study were examined statistically using the "paired t-test" to estimate the variance within sampler type and between sampler types.

The results of the within sampler comparison show that, at a 95% confidence level, there is no significant difference between the results obtained by two samplers of the same type for any parameter with the exception of rainfall amount for the F samplers and H_3O^+ with the S sampler. A breakdown of the data by rainfall amount, which will be discussed later, revealed that the significant difference for the F sampler occurred during heavier rainfalls, indicating that spillage may be a problem here. The H_3O^+ difference for the S sampler is at present not clear.

For the between sampler comparison, the F and S samplers were compared to the A samplers as it was felt that this sampler type was less prone to extraneous contamination and thus gave the "truest" results. Several differences were noted, as illustrated for selected parameters in Figure 3. Both the F and S samplers showed significant differences from the A sampler for a number of soil related parameters such as calcium and magnesium as well as for a number of non-soil related parameters such as hydrogen ion, sulphate and nitrate. Other parameters showing significant differences are potassium and sodium. There were no significant differences found between samplers for ammonia, conductivity and rainfall amount. The S sampler gave better agreement for all parameters with the A sampler as reflected by lower t values.

The observed differences are almost certainly due to dry contamination. The effect of this dry contamination on the H^+ concentration would depend

FIGURE 3: BETWEEN SAMPLER VARIATION

COMPARISON		SO_4^{2-}	NO_3^-	H^+	NH_4^+	Ca^{2+}	Mg^{2+}
A vs F	(1)	S	S	S	NS	S	S
	(2)	5.11	4.67	3.13	1.94	4.60	3.93
	(3)	26	26	26	26	26	27
A vs S	(1)	S	S	S	NS	S	S
	(2)	4.07	3.75	2.29	1.37	3.80	3.11
	(3)	26	26	26	26	25	27

(1) Significant (S) or not significant (NS) at 95% confidence level

(2) Calculated value of t

(3) No. of events

on whether the contaminating compound formed a base or acid in solution. Also a compound containing sulphate, such as $MgSO_4$ would also affect the sulphate concentration. Another source of sulphate contamination would be the dry deposition and subsequent oxidation of sulfur dioxide.

The ratio of hydrogen ion concentration in the F and S samplers compared to the hydrogen ion concentration in the A sampler is averaged in Figure 4. It can be seen that hydrogen ion concentration in the F or S sampler is, on average, only 88 and 85% respectively of that found in the A sampler, however, the standard deviation indicates the considerable variation in these figures.

No significant difference in rainfall recovery was found between the A and F and A and S samplers. However, the average rainfall measured by the three samplers is different from that measured by the standard tipping bucket rain gauge as illustrated in Figure 5. The A sampler results are on average close to those obtained with the tipping bucket gauge, differing by only 3%. However, there is considerable variation in these results so this should only be used as a comparison guide.

Concentration ratio plots were prepared for each parameter. The ratios were found to vary substantially from 1.0, and are particularly bad for the soil related elements Ca^{2+} and Mg^{2+} , especially where the observed concentrations were near the detection limit for these parameters in the A sampler, and thus only a small amount of contamination would be required to make the ratio much greater than 1.0.

Matrices of correlation coefficients between each parameter measured were calculated for the three types of sampler for all events. For this study, the data obtained for the Aerochem Metrics sampler are probably the best representation of the parameters in precipitation of the three samplers

FIGURE 4: RATIOS OF H⁺ CONCENTRATION

Ratio	(H ⁺) In Sampler 'X'	
	(H ⁺) In Aerochem Metrics	

	<u>F_{av}/A_{av}</u>	<u>S_{av}/A_{av}</u>
Average	0.88	0.85
SD	0.74	0.56

FIGURE 5: RAINFALL RECOVERY RATIOS

<u>A/TB</u>	<u>F/TB</u>	<u>S/TB</u>
1.03	1.21	1.12

Recorded rainfall ranged from 0.3 to 35.3mm for 32 events.

tested, as the potential for contamination is the least for this type of sampler. The correlation matrix for this sampler is illustrated in Figure 6.

Examination reveals some expected and some surprising results. Some of the expected good correlations found are correlations between H^+ , SO_4^{2-} , NO_3^- , between Ca^{2+} and Mg^{2+} , Na^+ , Cl^- . Surprising correlations are the reasonable correlation between Ca^{2+} and SO_4^{2-} , and the poor correlation between NH_4^+ and H^+ , SO_4^{2-} , NO_3^- . However, notwithstanding the above observations, the correlation matrices for the F and S samplers were found to be significantly different from the A sampler, as found in the "t-test" comparisons.

To try and rationalize the results obtained with different samplers, the whole data set was divided into subsets. These are: events with rainfall greater than or equal to 2.8mm, events with rainfall less than 2.8mm, events where the product of the average wind speed during the dry period times the fraction of the sampling period which was dry was less than or equal to 11, and similarly for greater than 11. The latter division is a form of contamination index. These subsets were chosen to see if any relationship existed between:

- a) the quantity of rain and the observed variance within and between sampler types
- b) The potential for contamination during dry periods and the observed variance within and between sampler types.

The within and between sampler variations were again examined using the paired "t-test". Within sampler variation shows that both the A and F samplers showed marginally significant difference in volume collected during higher rainfall periods. (i.e. $\geq 2.8\text{mm}$, < 11 contamination index).

FIGURE 6: AEROCHEM METRICS SAMPLER
CORRELATION COEFFICIENT MATRIX - ALL EVENTS

	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+
H^+									
NO_3^-	.64								
SO_4^{2-}	.67	.71							
NH_4^+	.34	.58	.50						
Cl^-	-.05	.35	.26	.04					
F^-	.01	.39	.34	.20	.30				
Cond	.93	.86	.92	.84	.16	.23			
Ca^{+2}	.01	.33	.56	-.06	.41	.32	.07		
Mg^{+2}	-.03	.25	.47	-.07	.44	.31	.01	.94	
Na^+	-.15	.19	.37	-.21	.64	.18	-.03	.56	.47
K^+	-.12	.21	.40	.44	.23	.25	.40	.54	.22
									.32

Between sampler variation showed significant differences, particularly for the S sampler during events when precipitation was low ($<2.8, >11$) for the parameters, H^+ , SO_4^{2-} , Ca^{2+} , Na^+ , K^+ , and rainfall amount whereas for high precipitation ($\geq 2.8, <11$) no significant differences were observed. This indicates the effect of dry deposition during periods of no rain.

To further illustrate these effects of dry deposition, Figure 7 shows the correlation matrix for events where shorter dry periods and lighter winds occurred, thus dry contamination is expected to be a minimum. We can see, for example, that the NH_4^+ vs H^+ correlation has increased from 0.34 to 0.82, and the Ca^{2+} vs SO_4^{2-} correlation has decreased from 0.56 to 0.37. Other parameters show similar changes. However, as illustrated in Figure 8, for events where longer dry periods and higher winds occurred, the NH_4^+ vs H^+ correlation disappears and in fact becomes negative, whereas the Ca^{2+} vs SO_4^{2-} correlation increases from 0.56 to 0.92. This gives a very clear demonstration that dry contamination is occurring. Similar effects are seen for other parameters. It should also be noted that these results are for the A sampler, the least affected by dry contamination. This suggests that this can be a serious problem even for automatic samplers and that for these conditions, what is measured is a complex combination of precipitation, dry deposition or contamination and evaporation. It should be reiterated that these effects are more marked for the F and S samplers.

FIGURE 7: AEROCHM METRICS SAMPLER
CORRELATION COEFFICIENT MATRIX - LOW CONTAMINATION INDEX (<11)

	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+	Vol
H^+											
NO_3^-	.75										
SO_4^{2-}	.96	.76									
NH_4^+	.82	.90	.84								
Cl^-	-.01	.20	-.12	.21							
F^-	.22	.53	.21	.23	-.03						
Cond	.97	.89	.97	.88	.12	.39					
Ca^{+2}	.35	.00	.37	.11	-.25	-.11	-.08				
Mg^{+2}	-.16	-.04	-.12	-.02	-.07	-.15	-.16	.97			
Na^+	-.17	-.03	-.06	-.18	.04	-.15	.01	-.10	-.05		
K^+	.56	.42	.49	.51	-.38	.17	.54	-.07	-.59	-.41	
Vol	.13	-.53	.07	-.27	-.24	-.39	-.17	-.34	-.40	-.17	.36
	H^+	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

FIGURE 8: AEROCHM METRICS SAMPLER
CORRELATION COEFFICIENT MATRIX - HIGH CONTAMINATION INDEX (>11)

NO_3^-	.45										
SO_4^{2-}	.28	.64									
NH_4^+	-.37	.04	.08								
Cl^-	.08	.63	.70	-.09							
F^-	-.17	.13	.50	.10	.58						
Cond	.77	.81	.70	.76	.42	-.06					
Ca^{+2}	.28	.71	.92	-.18	.76	.59	.58				
Mg^{+2}	.34	.61	.86	-.18	.80	.72	.58	.92			
Na^+	.08	.50	.68	-.25	.79	.18	.40	.68	.62		
K^+	-.31	.34	.48	.63	.30	.30	-.24	.38	.13	.22	
Vol	.00	-.26	-.62	-.23	-.62	-.41	-.46	-.48	-.50	-.52	-.42
	H^+	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	F^-	Cond	Ca^{+2}	Mg^{+2}	Na^+	K^+

CONCLUSIONS

The conclusions of the study are:

- The A sampler performed best of the three tested
- The F and S type samplers yield significantly different results from the A sampler for a number of parameters
- The S sampler was in better agreement than the F sampler
- The S sampler was the simplest to use
- The A sampler has a rain catch efficiency close to the tipping bucket rain gauge
- Differences observed between the results appear to be due to dry contamination
- Division of the data set according to rainfall amount and a contamination index support the above conclusion
- Evaporation does not appear to be a problem in 24 hour sampling.

REFERENCES

1. R. L. Berry, D. M. Whelpdale, H. A. Wiebe, "An Evaluation of Collectors for Precipitation Chemistry Sampling", Presented at the WMO Meeting on Wet and Dry Deposition, Atmospheric Environment Service, Downsview, Ontario, November 1975.
2. J. N. Galloway, G. E. Likens, Water, Air and Soil Pollution, 6, 241 (1976)
3. J. N. Galloway, G. E. Likens, Tellus, 30, 71 (1978)
4. L. J. Granat, Great Lakes Research, 2(1), 42 (1976)
5. MAP3S Precipitation Intercomparison Study, MAP3S Progress Report for FY1977 and 1978.

DEFINITION OF THE SPHERE OF INFLUENCE OF THE MINING ACTIVITIES
AT ELLIOT LAKE, ONTARIO, BY ASSESSMENT OF THE LEVELS OF URANIUM
AND OTHER ELEMENTS IN LICHENS AND MOSSES

E. Nieboer*, D.H.S. Richardson, L. Boileau, P.J. Beckett and
E.D. Hallman

Faculty of Science and Engineering,
Laurentian University, Sudbury, Ontario
P3E 2C6 and

*Department of Biochemistry, McMaster University,
Faculty of Health Sciences, 1200 Main Street W.,
Hamilton, Ontario L8N 3Z5

1. INTRODUCTION

Lichens and mosses are valuable plants for monitoring the environment as they accumulate elements by trapping particulates (tiny dust particles) as well as by absorption of dissolved minerals (Nieboer et al., 1978). These plants, collectively called cryptogams, do not have elaborate root systems. Consequently, uptake from the substratum is minimal in most species compared to the accumulation through the plant body (called the thallus) by dry deposition of dust and from solids and electrolytes in rain and surface water (Nieboer et al., 1978; Svoboda and Taylor, 1979). In various parts of the world, lichens and mosses have been used to monitor the levels of more than 25 different elements in studies of environmental quality around smelters, manufacturing plants, and urban centres (e.g., Rao et al., 1977; Richardson et al., 1980; Nieboer and Richardson, 1980). However, lichens and mosses have not been used specifically for the monitoring of uranium until recently. Selected highlights of this new work are described in this report. An assessment of the accumulation of uranium and related elements in lichens and mosses indicates the feasibility to evaluate the sphere of influence of the uranium mining and milling operations in the town of Elliot Lake, Ontario.

2. EXPERIMENTAL APPROACH

Collection Sites

Lichen and moss samples were collected along a 54 km SSE macro-transect originating near the Elliot Lake mining and milling centres (Fig.1). Separate collections were also made along micro-transects (0-500 m) measured from potential sources including horizontal and vertical exhaust vents, tailing areas and mills (Fig. 2).

Collection of Material

Only the top living portions (3-4 cm) of lichen and moss clumps were collected to reduce the inclusion of debris and possible soil contamination. Composite samples were placed in paper bags, transported to the laboratory, and were dried and stored in these bags until used.

Cleaning of Samples

The collected lichens and mosses were soaked in distilled water and were then thoroughly washed under running distilled water. Debris and discoloured parts of the sample were removed. The washed samples were allowed to air dry and were subsequently crushed and ground in a mortar with a pestle using liquid nitrogen to facilitate the process. The resultant powder was passed through a 70-mesh stainless steel sieve, was oven dried at 80°C for 24 h, and was then stored in sealed vials which were kept in a desiccator until the analysis.

Elemental Analysis

Sample preparation. Two approaches were taken in readying the samples for analysis. For the determination of iron, nickel, lead and titanium, 2 g quantities of the powdered materials were pressed into pellets of 32 mm diameter. For improved durability and handling, a small

amount of wax was mixed in prior to pelleting. Additional details are provided in Tomassini *et al.*, 1976. The second approach was dictated by the low levels of uranium present in the lichen and moss samples. In this case, 5 g samples of ground material were ashed at 500°C. Subsequently, 30 mg of the ash were placed between two thin mylar sheets clamped onto a plastic sample holder suitable for the spectroscopic measurements.

Analytical procedure. Samples were analyzed for Fe, Ni, Pb, Ti and U by X-ray fluorescence spectrometry (XRF). In the case of the first four elements mentioned, a single standard pellet of known element content was used to calibrate the spectrometer after every seven samples. Additional detail is provided by Tomassini *et al.* (1976). A similar approach was taken for the uranium analysis. Standard ash samples were prepared by adding aliquots of solutions of this element to powdered samples of Cladonia rangiferina prior to ashing. The standard material had been collected on Manitoulin Island and contained no measurable uranium. For an independent check, ten of the analyzed ashed samples were subjected to analysis for uranium by neutron activation at the University of Toronto Slowpoke Neutron-activation Centre. Excellent agreement was obtained over the entire concentration range observed in our study (0 - 150 ppm. dry wt).

Statistical analysis. The analytical data for a total of 109 lichen and 98 moss samples including 36 cryptogamic samples from the Agnew Lake uranium mine vicinity, were subjected to statistical analyses using modified programs of the University of Pittsburgh Social Sciences Statistical Package (Nie *et al.*, 1975). All work was executed on the Laurentian University DEC 2020 computer.

3. RESULTS

Relative Accumulation Indices

For a number of mosses and lichens the ability to accumulate Fe, Ni, Pb, Ti and U relative to that observed for Cladonia rangiferina is compared in Table 1. It is evident that Cladonia mitis and Cladonia rangiferina had similar metal contents. Pakarinen *et al.* (1978) have indeed predicted low variability for the trace elemental contents for members of the genus Cladonia. The Stereocaulon sp. collected accumulated up to three times as much as the Cladonia species. Similar differences in affinity were also seen for the mosses. Accumulation tendencies of the Sphagnum and Polytrichum species in Table 1 were of comparable magnitudes, although somewhat weaker than that observed for Cladonia rangiferina. In contrast, the Pleurozium and Dicranum species both exhibited relative accumulation indices of about 2.

Differences in accumulation ability of lichens appear to be correlated with thallus morphology (smooth *versus* rough and pitted surfaces; and loosely *versus* tightly packing of the thallus). Similar macro-morphological arguments have been presented for mosses (Pakarinen and Rinne, 1979). In addition, microscopic examination of lichen tissue have revealed considerable variation in the volume of free space, and thus differences in the number and size of interstitial crevices available for particulate trapping (Richardson and Nieboer, 1980; Nieboer and Richardson, 1980).

We may conclude from the data summarized in Table 1 that choice of species is an important principal in environmental assessment work with lichens and mosses. It is helpful to know when planning future field sampling programs that Cladonia mitis and Cladonia rangiferina samples are

complementary. Similarly, Pleurozium schreberi and the Dicranum species are interchangeable, as well as Polytrichum commune and the Sphagnum species.

Metal Distribution Patterns

The data plotted in Figures 3 and 4 reveal an exponential dependence of the uranium content with distance for cryptogams. For the lichen Cladonia rangiferina a rapid decline in uranium levels coincided with the increase in distance between the collection site and the Elliot Lake mining and milling operations. Data for Cladonia mitis also conformed to the illustrated curve. Furthermore, a curve of similar shape was observed for Pleurozium schreberi, although as predicted from the relative accumulation indices in Table 1 the uranium levels were generally higher at all sites along the transect for this moss. Typical uranium versus distance curves over short distances from emission sources are shown in Figure 4. For these micro-transects, the fall-off patterns with distance of the Fe, Ti and Pb contents resembled those shown for uranium. No strong distance dependence was discerned for Ni.

It is concluded from the above and other data (Richardson et al., 1979) that the sphere of influence of vertical exhaust vents extends up to 300 m, while the greatest effect along the Elliot Lake macro-transect is apparent within the first 10 km.

Particulate Trapping

Unequivocal evidence for the accumulation of inorganic dust in lichens and mosses is provided in Figure 5. Since the shapes of the curves in Figures 4 and 5 are similar, it is concluded that uranium

deposition parallels the fall-out of dust. Similar conclusions may be drawn for Fe, Pb and Ti. Consequently, the amount of non-combustible inorganic residue present in cryptogams provides a clear indication of the severity of dust deposition.

Iron-Titanium Pollution Index

In Fig. 6, the iron content of all Cladonia rangiferina and Cladonia mitis samples are plotted against the corresponding titanium levels. The displayed data may be fitted arbitrarily to two linear segments with slopes of $6.9 \mu\text{g Fe}/\mu\text{g Ti}$ (lower portion) and $15.3 \mu\text{g Fe}/\mu\text{g Ti}$ (upper segment). As a first approximation, points describing the lower segment would fall on the distance-independent portions of curves like those exhibited in Figure 7. Thus these data correspond to collection sites not influenced seriously by a nearby point source. As might be expected, data defining the upper and steeper segment in Figure 6 may be correlated with collection sites in the immediate vicinity of exhaust vents ($< 200 \text{ m}$). Hence these data points correspond to the steeply rising portions of the Fe/Ti ratio versus distance curves in Figure 7.

Values of the slopes for Fe versus Ti content plots between 6.5 and 7.2 have been predicted on the basis of the average composition of the earth crust, including data for the Pre-cambrian Canadian Shield. Indeed, such Fe/Ti slope values have been found for particulates in lichens from "non-polluted" sites in Canadian Arctic and the Province of New Brunswick (Nieboer et al., 1978). The observed slope of 6.9 for the lower segment in Figure 6 is thus taken to be diagnostic of background dust relatively free of either enrichment of iron or titanium. Conversely,

the slope of 15.3 for the upper segment in Figure 6 would appear to signal a local enrichment of iron. Indeed, evaluations of the Fe/Ti ratio for Elliot Lake tailings and ores based on chemical analysis data yield values near 15 (Rasberry and Gorber, 1978; Raicevic, 1979). It should be emphasized that the Fe/Ti slope values are not equivalent to the observed Fe/Ti content ratios for individual samples because of the non-zero y-intercept values of the linear segments in Fig. 6 (see Nieboer et al., 1978). Enhancement of Fe/Ti ratios have also been observed for lichen samples collected in the vicinity of the Sudbury nickel smelting operations, a known source of iron emissions (Nieboer et al., 1978).

Inter-Elemental Comparisons

An examination of Pearson correlation coefficients for inter-elemental comparisons revealed that for all sites examined and for all species of lichens and mosses collected, there was a strong linear correlation ($p < 0.001$) between the iron and titanium levels, as well as for the uranium and lead contents. Additional strong linear correlations were observed for samples collected in the vicinity of direct primary sources, such as exhaust vents, for the pairs uranium and iron, and titanium and uranium. The correlation between nickel and uranium levels was only weakly significant ($p < 0.01$). The prominence of U, Fe, Ti and Pb, and the lesser importance of Ni, are consistent with the known composition of the Elliot Lake ores and tailings (J.A. Robertson, 1968; S.M. Roscoe, 1969; Murray and Moffett, 1977; Rasberry and Gorber, 1978; Raicevic, 1979). This agreement is interpreted as evidence that the elemental content of lichens and mosses from the Elliot Lake area correctly characterize the environmental impact of the mining and milling operations there.

4. PRESENT AND FUTURE WORK

The work completed to date has illustrated the real potential of employing lichens and mosses in environmental assessments of impingement patterns from the Elliot Lake mining/milling operations. Further sampling of Cladonia rangiferina and Pleurozium schreberi was completed this past summer. Collections along transects from active dry- and wet-tailing sites were emphasized. Appropriate analysis of this newly collected material is underway.

Good progress is being made in the development of an atomic absorption spectrophotometric (AA) method suitable for the routine analysis of uranium at sub-microgram level. The approach taken consisted of lining the graphite tube of the electrothermal furnace with tantalum foil and employing K^+ as a deionizer. Both of these steps have improved the sensitivity, and permit routine determinations with a detection limit < 40 ng/ml using a 20 μl sample. Additional improvements in sensitivity and precision are expected as small technical difficulties in the design and manufacture of the tantalum inserts are overcome. The AA method is ideal for laboratory uranium uptake and toxicological studies. Preliminary work with lichens indicates that UO_2^{2+} replaces extracellular Ca^{2+} , and that the neutral liganded forms of the uranyl species are apparently taken up intracellularly. Damage to plant tissue is being assessed by measuring the degree of K^+ efflux into the uranium incubation medium and by monitoring changes in the ^{14}C photosynthetic fixation rates after the metal-uptake step.

Another promising development has been the identification of radioisotopes in cryptogamic samples by alpha spectroscopy. A typical alpha spectrum is shown in Fig. 8 and was derived from a sample of the moss Polytrichum commune. Many of the daughter isotopes for both

the Uranium-238 and Thorium-232 series are identified. The experimental procedure involves fusing the vegetation ash with potassium pyrosulphate, removal of the transition metals by electrolysis in 0.3 M sulphuric acid, and electroplating of the radioisotopes from mildly acidic solution onto stainless steel α -counting planchets. To date, excellent uranium recoveries have been observed for synthetic aqueous standards. Improvements in the final electrochemical plating process are required before routine quantitation of radioisotope concentrations is possible in cryptogamic samples. Additional method development is expected to overcome these deficiencies in quantitative recovery work.

5. CONCLUSIONS

It has been demonstrated that the element content of lichens and mosses clearly reflect local impingement and atmospheric deposition patterns. The systematic decrease in non-combustible inorganic dust and in indicator elemental concentrations with distance along macro-transects from the Elliot Lake mining and milling operations, and along micro-transects from primary sources such as exhaust vents, allows an assessment of the effective sphere of influence. We may also conclude from the preliminary results described in this paper that the monitoring of the major elements Fe, Pb, U and Ti can be a good indicator of the distribution of radioisotopes. The established fall-out patterns of the major elements will no doubt be useful in the planning of detailed radioisotope studies.

ACKNOWLEDGEMENTS

Professional assistance from Miss Pat Lavoie, Miss Dilva Padovan and Miss Emélie Lamothe is gratefully acknowledged. Appreciation is also extended to Mr. C. Chakriavati (Denison Mines) and Mr. A. Vivyunka (Rio Algom Mines) for their cooperation in arranging the field collections. Assistance in the computer analysis from Dr. Roger Pitblado, Department of Geography, Laurentian University is gratefully acknowledged. And finally, we wish to thank Professor K. Winterhalder, Department of Biology, Laurentian University for helpful discussions, and Dr. David Balsillie, Chief, Air Quality Technical Support Section, Ministry of the Environment, Sudbury, Ontario, for his able assistance and encouragement in his capacity as project liaison officer.

REFERENCES

Murray, D. and Moffett, D. 1977. Vegetating the uranium mine tailings at Elliot Lake, Ontario. *J. Soil Water Conserv.* 32: 171-174.

Nie, N.H., Hull, C.H., Jenkins, J.G., Steinbrenner, K. and Bent, D. 1975. Statistical package for the social scientist, 2nd ed. McGraw-Hill, New York.

Nieboer, E. and Richardson, D.H.S. 1980. Lichens as monitors of atmospheric deposition. In *Atmospheric input of pollutants to natural waters*, edited by S.J. Eisenreich. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan. In Press.

Nieboer, E., Richardson, D.H.S. and Tomassini, F.D. 1978. Mineral uptake and release by lichens: an overview. *Bryologist* 81: 226-246.

Pakarinen, P. and Rinne, R.J.K. 1979. Growth rates and heavy metal concentrations of five moss species in paludified spruce forests. *Lindbergia* 5: 77-83.

Pakarinen, P., Mäkinen, A and Rinne, R.J.K. 1978. Heavy metals in Cladonia arbuscula and Cladonia mitis in eastern Fennoscandia. *Ann. Bot. Fennici* 15: 281-286.

Raicevic, D. 1979. Decontamination of Elliot Lake uranium tailings. *CIM Bulletin* (August issue): 1-7.

Rao, D.N., Robitaille, G. and Leblanc, F. 1977. Influence of heavy metal pollution on lichens and bryophytes. *J. Hattori Bot. Lab.* 42: 213 -239.

Rasberry, J.M. and Gorber, D.M. eds. 1978. Environmental assessment of the proposed Elliot Lake uranium mines expansion. Report by J.F. MacLaren Ltd., in 4 volumes.

Richardson, D.H.S. and Nieboer, E. 1980. Surface binding and accumulation of metals in lichens. In *Cellular interactions in symbiosis and parasitism*, edited by C.B. Cook, P.W. Pappas and E.D. Rudolph. Ohio State University Press, Columbus, Ohio, pp.75-94.

Richardson, D.H.S., Beckett, P.J. and Nieboer, E. 1980. Nickel in lichens, bryophytes, fungi and algae. In *Nickel in the environment*, edited by J.O. Nriagu. John Wiley and Sons, Inc., New York, pp.367-406.

Richardson, D.H.S., Nieboer, E., Beckett, P.J., Boileau, L., Lavoie, P. and Padovan, D. 1979. The levels of uranium and other elements in lichens and mosses growing in the Elliot Lake and Agnew Lake areas, Ontario, Canada. Report to the Ontario Ministry of the Environment. 71 pp.

Robertson, J.A. 1968. Geology of Townships 149 and 150. Geological Report 57, Ontario Department of Mines (Ministry of Natural Resources), Toronto, Ontario, pp.76-125.

Roscoe, S.M. 1969. Huronian rocks and uraniferous conglomerates. Geological Survey of Canada Report 68-40, Department of Energy, Mines and Resources, Ottawa, Ontario.

Svoboda, J. and Taylor, H.W. 1979. Persistence of cesium-137 in arctic lichens, Dryas integrifolia, and lake sediments. *Arct. Alp. Res.* 11: 95-108.

Tomassini, F.D. 1976. The measurement of photosynthetic ¹⁴C fixation rates and potassium efflux to assess the sensitivity of lichens to sulphur dioxide, and the adaptation of X-ray fluorescence to determine the elemental content in lichens. M.Sc. Thesis, Laurentian University, Sudbury, Ontario.

Tomassini, F.D., Puckett, K.J., Nieboer, E., Richardson, D.H.S. and Grace, B. 1976. Determination of copper, iron, nickel and sulphur by X-ray fluorescence in lichens from the Mackenzie Valley, Northwest Territories, and the Sudbury District, Ontario. *Can. J. Bot.* 54: 1591-1603.

TABLE 1 Comparative Trace-element Levels in Lichens (L) and Mosses (M)

Ratios are computed for each species against the corresponding elemental content of Cladonia rangiferina. Only those sites where species occur in common with Cladonia rangiferina are used in calculation of the ratios. Ratios are expressed as mean \pm 1 standard error; values greater than 1.00 denote enhancement.

Species	Elemental ratio					Number of sites where both species occur in common
	Iron	Nickel	Lead	Titanium	Uranium	
<u>Cladonia mitis</u> (L)	1.07 \pm 0.05	0.95 \pm 0.03	0.90 \pm 0.05	1.10 \pm 0.05	0.97 \pm 0.11	22
<u>Stereocaulon</u> sp. (L) ^a	2.66 \pm 0.32	1.92 \pm 0.27	1.27 \pm 0.06	3.43 \pm 0.38	2.22 \pm 0.21	6
<u>Dicranum</u> spp. (M) ^b	2.51 \pm 0.81	2.73 \pm 0.60	2.33 \pm 0.72	1.95 \pm 0.56	1.48 \pm 0.09	4
<u>Pleurozium schreberi</u> (M)	1.69 \pm 0.11	1.84 \pm 0.15	1.94 \pm 0.19	1.38 \pm 0.09	1.91 \pm 0.18	13
<u>Polytrichum commune</u> (M)	0.77 \pm 0.15	1.09 \pm 0.15	0.95 \pm 0.16	0.80 \pm 0.24	1.02 \pm 0.19	10
<u>Sphagnum</u> spp. (M) ^c	0.87 \pm 0.24	1.07 \pm 0.13	1.02 \pm 0.13	0.76 \pm 0.19	1.07 \pm 0.51	10

a Likely Stereocaulon paschale but taxonomically a difficult group in which to differentiate species; L denotes lichen.

b Two species: Dicranum viride and Dicranum montanum, often mixed together; M denotes moss.

c Five species; mostly of the Sphagnum acutifolium group

LEGENDS TO FIGURES

Fig. 1. Area map indicating collection sites for the Elliot Lake macro-transect.

Fig. 2. Area map showing micro-transect collection sites in the vicinity of the Rio Algoma and Denison Mining and Milling operations. Collections were made at four other sites located south of the area shown. Two sites were adjacent to Horn Lake, and the other pair were close to the Nordic 'Old' tailings area.

The symbols are defined as follows:

—, Road or highway; 0, Water; ----, Tailing;

■, Horizontal mining exhaust vent; □, Vertical mining exhaust vent; •••, Micro-transect collection site;

■, Building.

Fig. 3. Lichen uranium content of Cladonia rangiferina as a function of distance along the Elliot Lake macro-transect.

Fig. 4. Uranium content of some lichens and mosses as a function of distance from the vertical exhaust on Knowles Island (site 1, Fig. 2).

Fig. 5. Percentage content of non-combustible, inorganic ash in cryptogams as a function of distance of the collection site from the Quirke-1E Mine horizontal exhaust vent (site 4, Fig. 2).

Fig. 6. The relationship between the iron and titanium contents of Cladonia rangiferina and Cladonia mitis. Data from all macro- and micro-transects are represented. The slopes of

Fig. 6. continued.....

the arbitrarily placed segments evaluated by linear regression were 6.9 (lower segment) and 15.3 (upper segment).

Fig. 7. Variation of the iron/titanium ratio for lichen and moss samples with distance of the collection site from the Quirke-1E Mine horizontal exhaust vent (site 4, Fig. 2).

Fig. 8. Alpha spectrum for a sample of Polytrichum commune collected near a mill. The various radioisotopes present correspond to the Uranium-238 and Thorium-232 decay schemes. The 1024 channel analyzer was adjusted to a resolution of 11.0 keV per channel and was calibrated with an Americium-241 standard source.

MACRO-TRANSECT

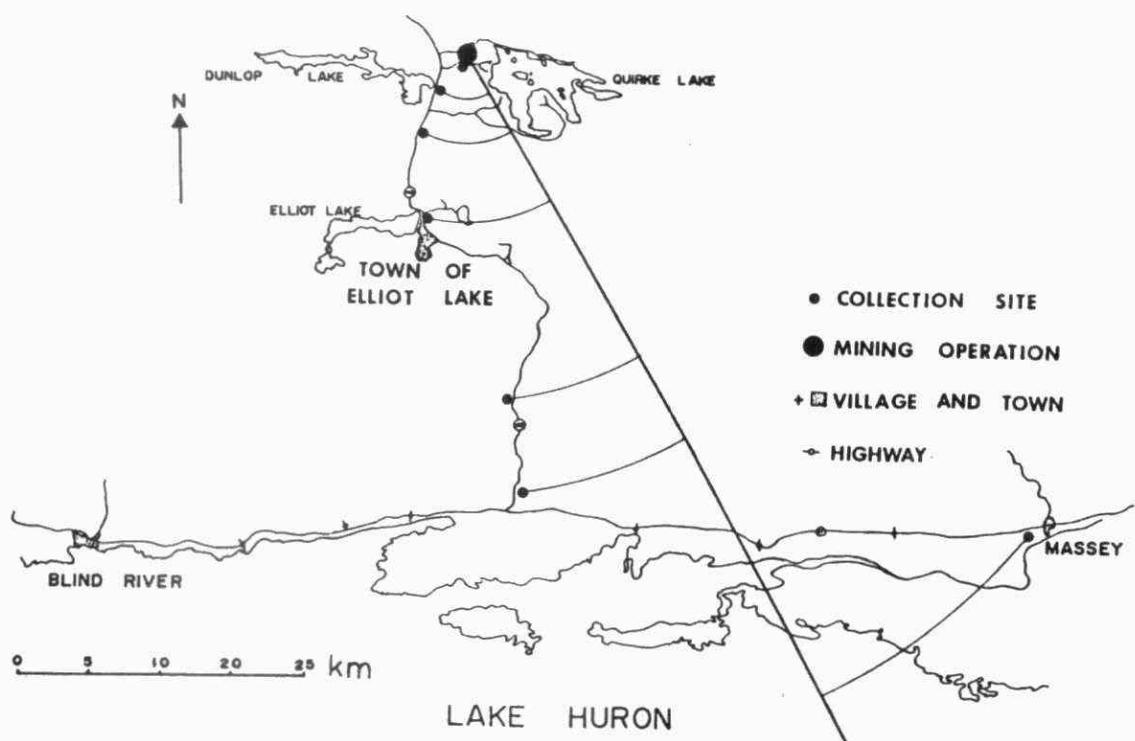


Figure 1 (Niebaer et al.)

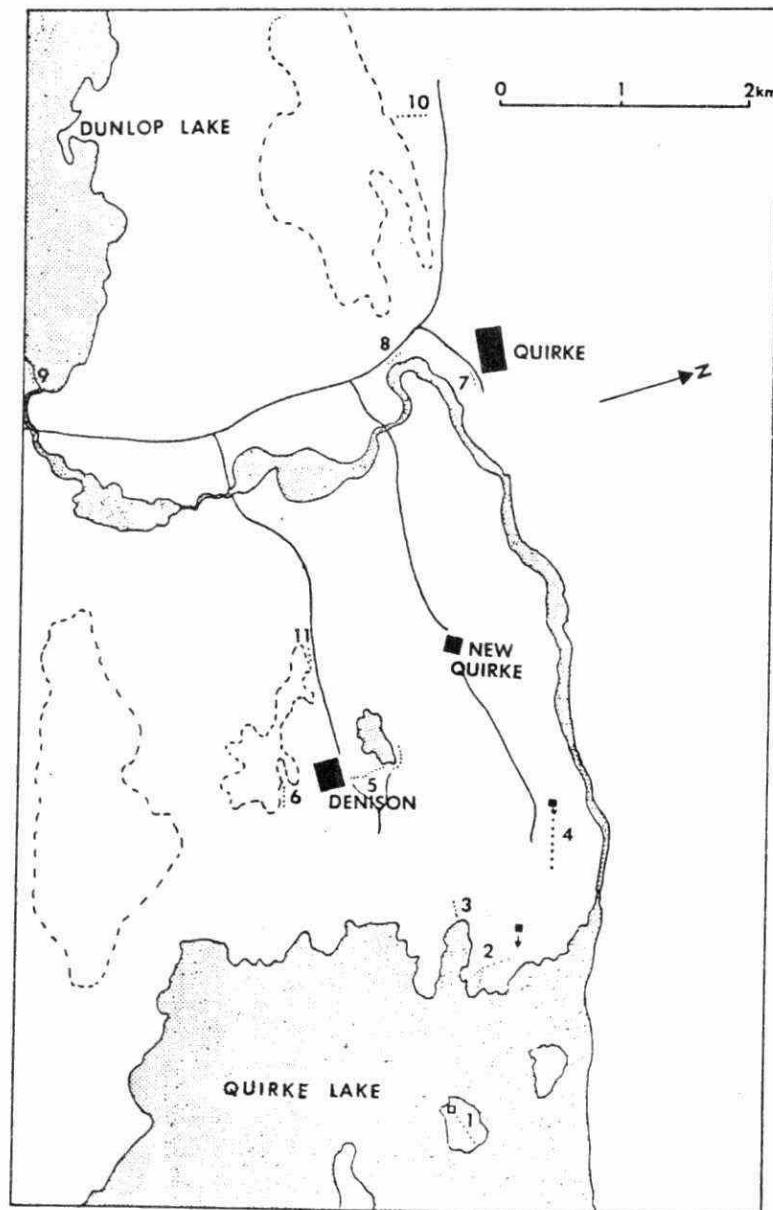


Figure 2 (Nieboer et al.)

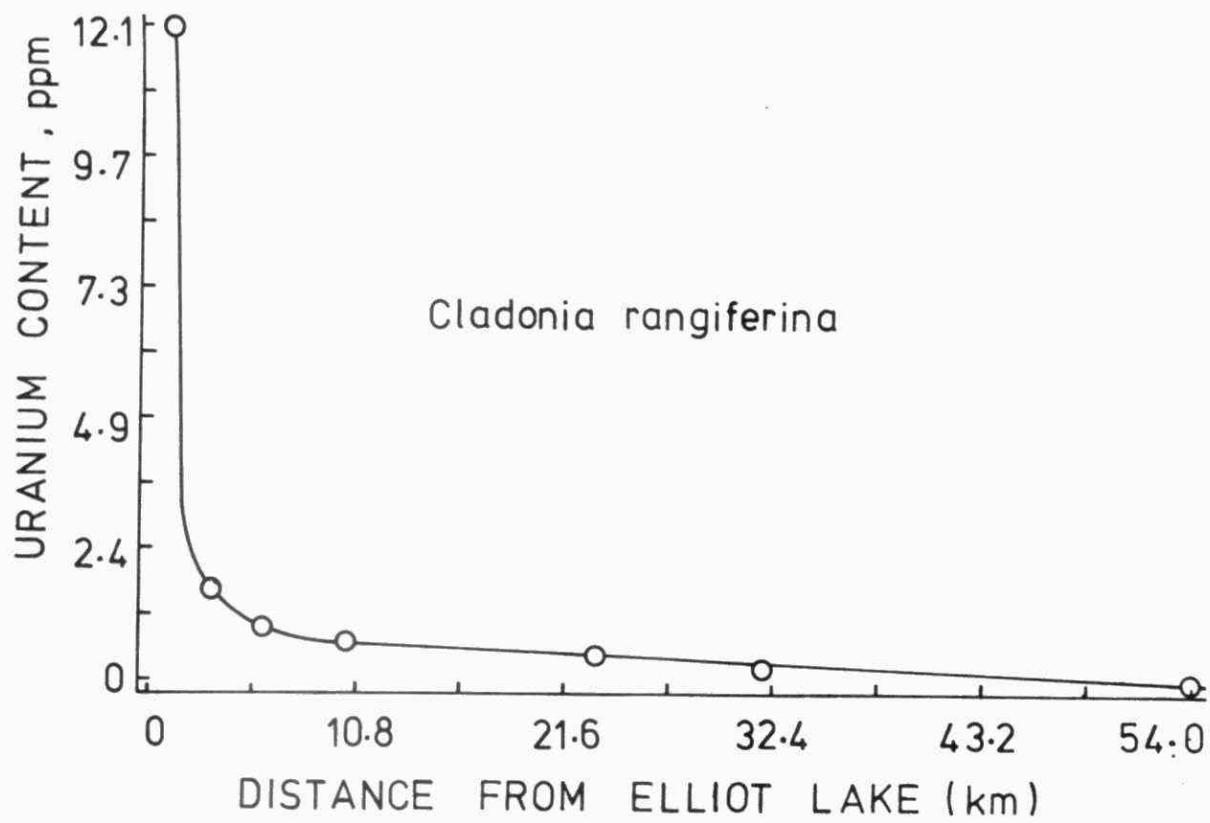


Figure 3 (Nieboer et al.)

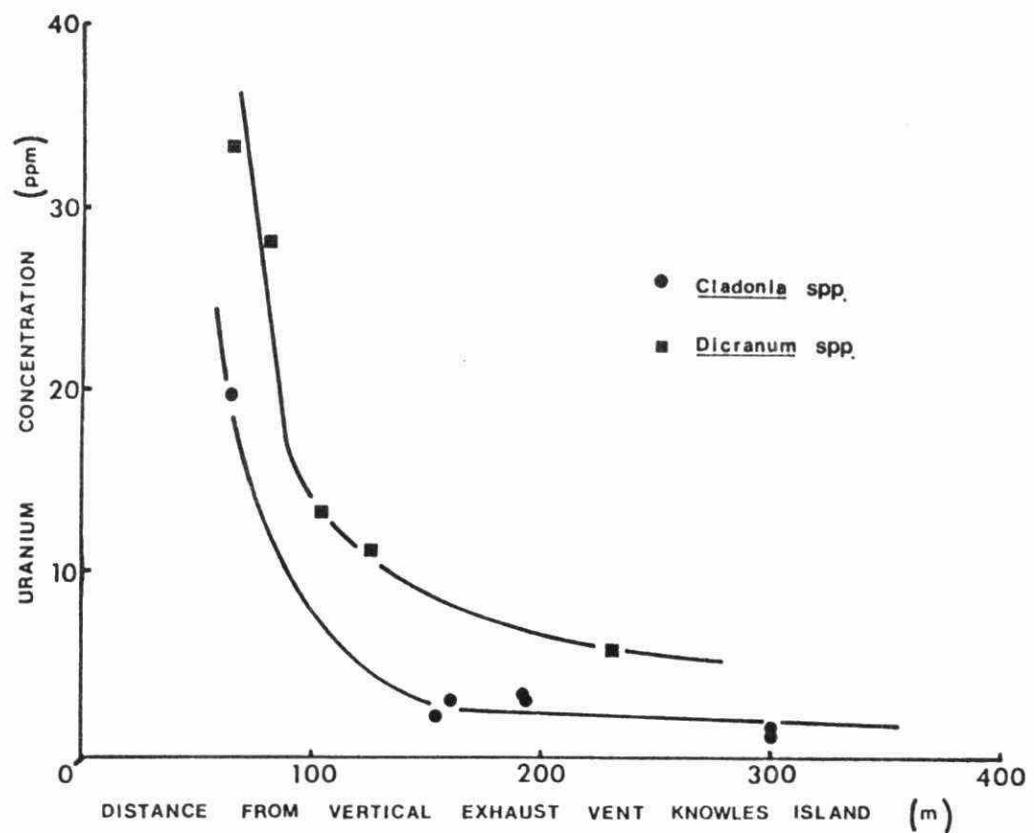


Figure 4 (Nieboer et al.)

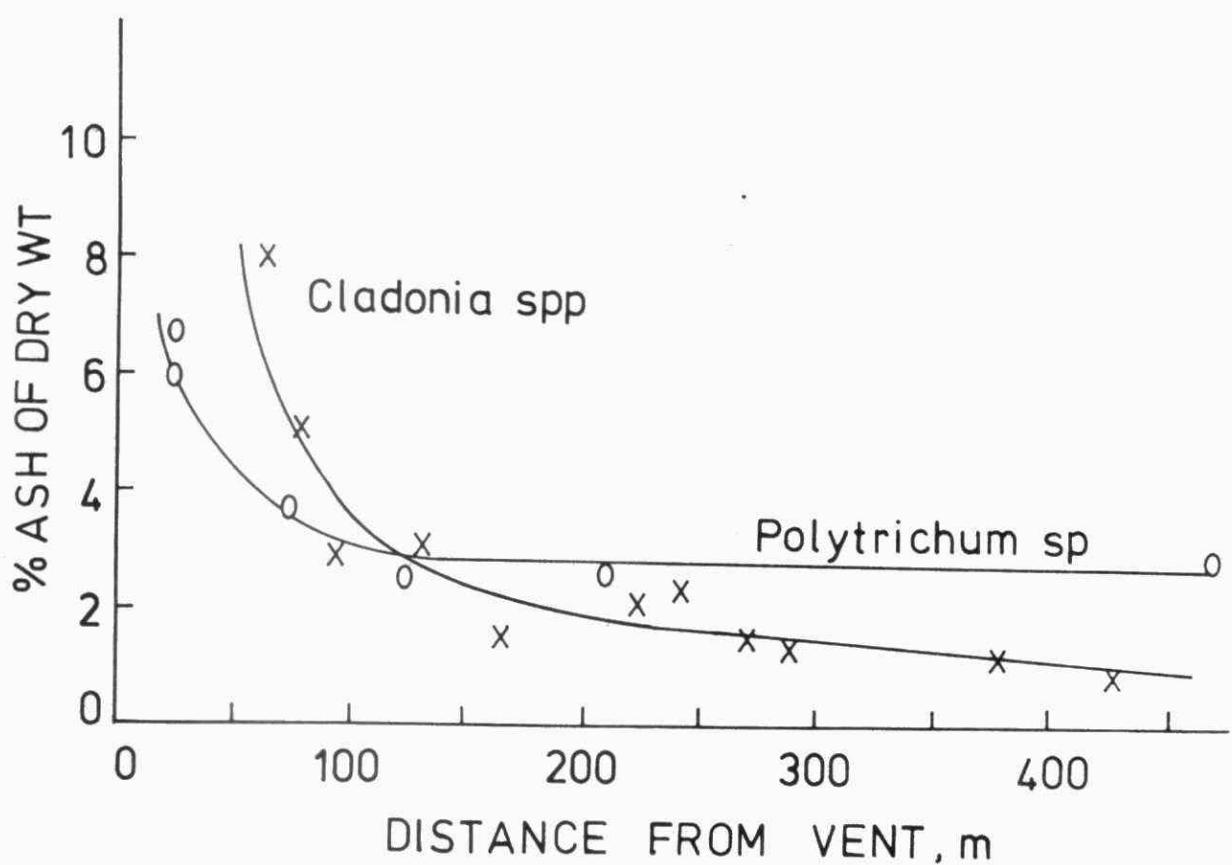


Figure 5 (Nieboer et al.)

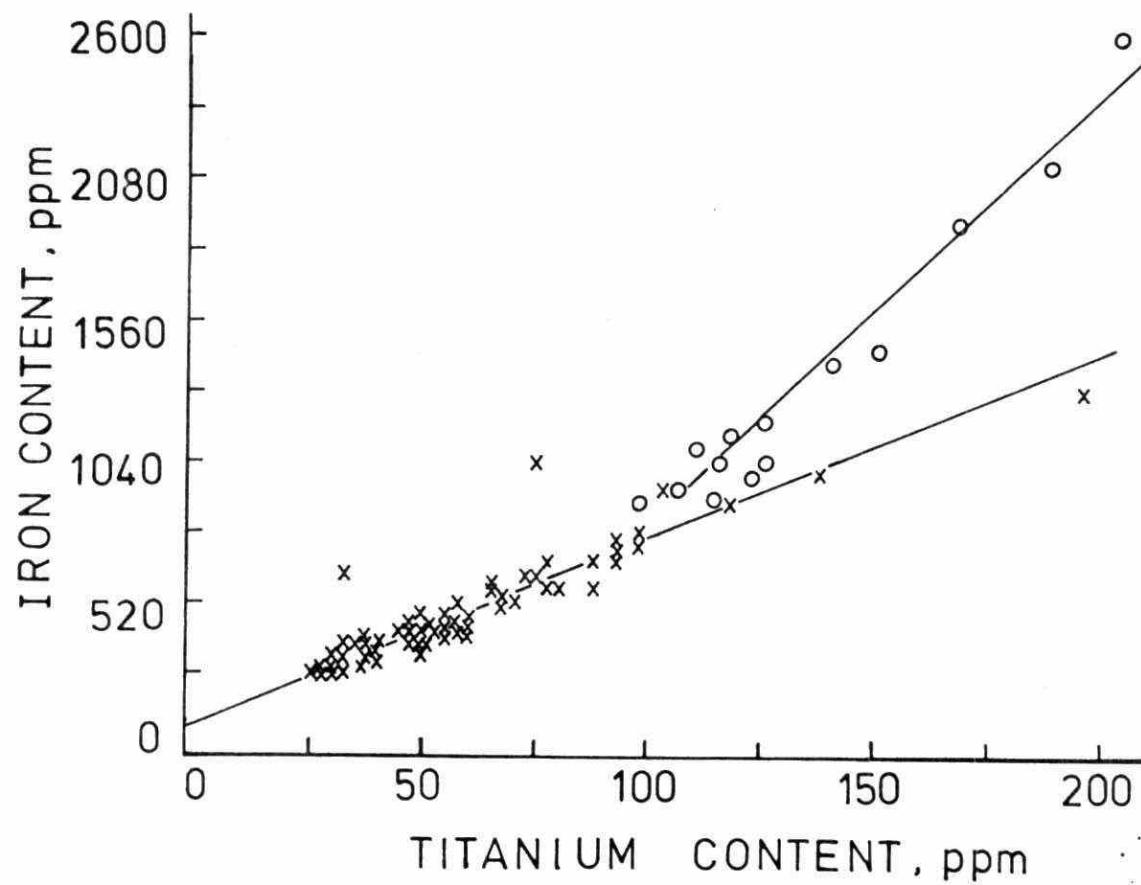


Figure 6 (Nieboer *et al.*)

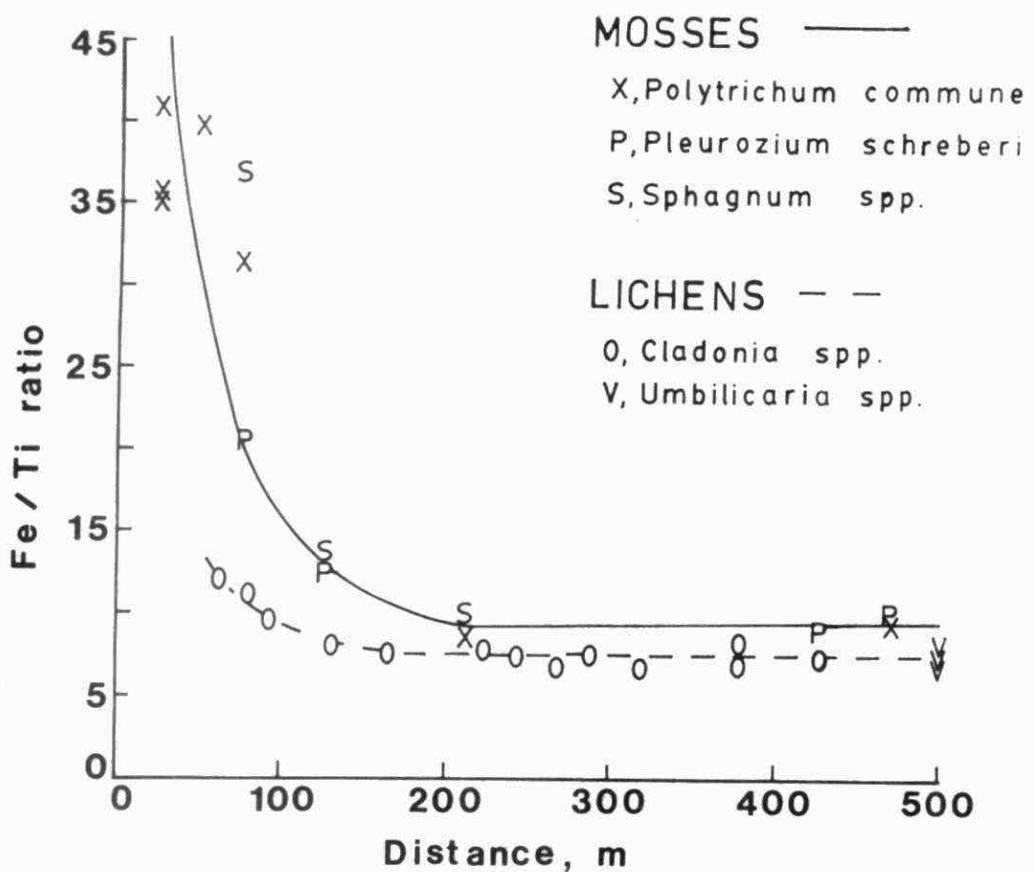


Figure 7 (Nieboer et al.)

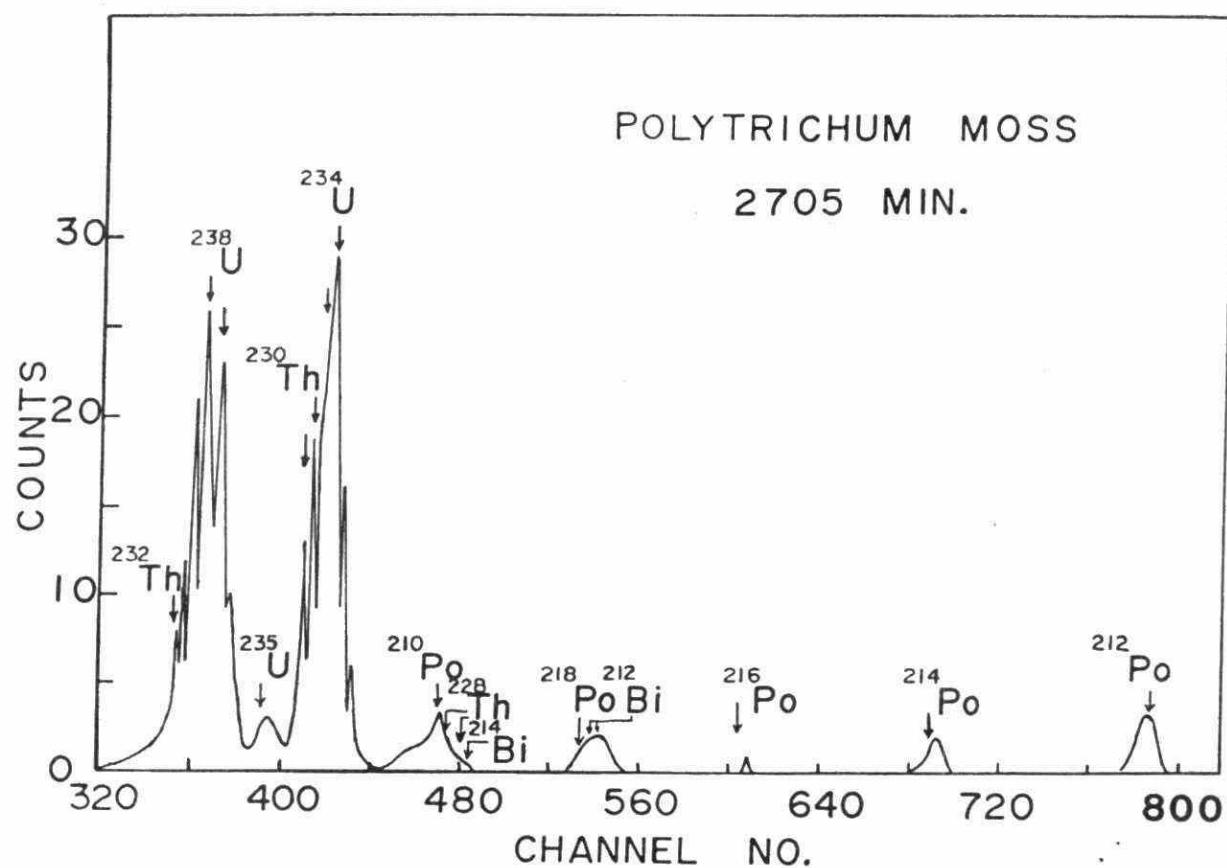


Figure 8 (Niebler et al.)

ACID RAIN - AN OVERVIEW

TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 25, 1980

E. W. PICHE

ABSTRACT

THIS PAPER WILL OUTLINE THE EVOLUTION OF THE ONTARIO GOVERNMENT'S RECOGNITION, CONCERN, ULTIMATE ACTIONS, AND OVERALL STRATEGY WITH RELATION TO THE ACIDIFICATION OF PRECIPITATION PHENOMENON. SPECIFICALLY, KEY TURNING POINTS FROM BOTH THE SCIENTIFIC AND THE EVOLUTIONARY VIEWPOINTS WILL BE MENTIONED. IN ADDITION, ONTARIO'S TECHNICALLY COMPREHENSIVE PROGRAM WILL BE REVIEWED.

INTRODUCTION

ATMOSPHERIC WATER IN EQUILIBRIUM WITH CARBON DIOXIDE THEORETICALLY WILL HAVE A PH OF 5.6. EXPERIMENTAL OBSERVATIONS MADE AS PART OF THE SUDBURY ENVIRONMENTAL AND LAKESHORE CAPACITY STUDIES OVER A PERIOD GREATER THAN FIVE YEARS, LED SCIENTISTS WORKING FOR THE ONTARIO MINISTRY OF THE ENVIRONMENT TO THE CONCLUSION THAT THE ACIDITY OF RAIN FALLING IN LARGE AREAS OF ONTARIO WAS FAR GREATER THAN THAT PREDICTED BY THE AFOREMENTIONED EQUILIBRIUM. IN FACT, IN AN AREA RANGING ROUGHLY FROM SUDBURY EAST TO KINGSTON AND SOUTH TO TORONTO, THE AVERAGE PH OF PRECIPITATION RANGES FROM 4.0 - 4.5.

THE PH SCALE IS A LOGARITHMIC SCALE USED TO REFERENCE AND COMPARE FREE HYDROGEN ION CONCENTRATIONS IN SOLUTION. THE SCALE RUNS FROM ROUGHLY 1.0 TO 14.0 WITH 7.0 BEING NEUTRAL, NUMBERS LESS THAN 7.0 INDICATING ACIDS AND THOSE GREATER THAN 7.0 INDICATING BASES. AN IMPORTANT FEATURE OF THIS SCALE IS THE FACT THAT A PH CHANGE FROM 7.0 TO 6.0 CORRESPONDS TO AN INCREASE IN ACIDITY OF 10 TIMES. A CHANGE OF PH FROM 7.0 TO 5.0 REPRESENTS A HUNDRED-FOLD INCREASE IN THE ACIDITY CONCENTRATIONS AND SO ON. TABLE ONE LISTS THE PH OF SOME COMMON MATERIALS.

TABLE ONE
PH OF COMMON MATERIALS

MATERIAL	PH
VINEGAR	2.2
APPLES	3.0
SAUERKRAUT	3.5
TOMATOES	4.2
CARROTS	5.0
SALIVA	5.7-7.1
MILK	6.6
HUMAN URINE	7.4
SEA WATER	8.3
0.1 M NH ₃	11.2

SOURCE: W. L. MASTERTON AND E. J. SLOWINSKI,
CHEMICAL PRINCIPLES (PHILADELPHIA, PA.: W. B. SAUNDERS Co.,
1969), p. 428.

CURRENTLY, IT IS FELT THAT THE REASON FOR THIS UNNATURAL ACIDITY CONCENTRATION IN PRECIPITATION IS THE FACT THAT, CONCOMITANT WITH INCREASES IN INDUSTRIAL ACTIVITY BY MAN OVER CONTINENTAL NORTH AMERICA IN THE PAST 25 YEARS, THERE HAVE BEEN SIGNIFICANT INCREASES IN EMISSIONS OF OXIDES OF NITROGEN AND SULPHUR. THE PRINCIPAL CONTRIBUTORS ARE FROM THE GENERATION OF ELECTRICITY BY THERMAL MEANS USING COAL AND OIL AS FUELS AND THE NON-FERROUS SMELTING INDUSTRY.

OF GREATER IMPORTANCE AND RELEVANCE TO THIS PHENOMENON, IS THE FACT THAT OVER THE PAST 15 YEARS, AS A CONSEQUENCE OF THE 1960'S DICTUM OF "THE SOLUTION TO POLLUTION IS DILUTION", A LARGE NUMBER OF VERY TALL, OF THE ORDER OF 500 FT. OR MORE, SMOKESTACKS HAVE BEEN ERECTED OVER EASTERN CONTINENTAL NORTH AMERICA IN AN ATTEMPT TO MEET GROUND LEVEL CONCENTRATION CRITERIA SET BY WELL-MEANING LOCAL REGULATING AGENCIES.

FURTHER, THE INSTALLATION OF ELECTROSTATIC PARTICULATE REMOVAL DEVICES HAS SEEMINGLY FURTHER EXACERBATED THE PROBLEM BY REMOVING FROM THE EMITTANTS, SOME INHERENT NEUTRALIZATION CAPACITY.

TOGETHER, THESE EVENTS HAVE CONTRIBUTED TO THE CURRENT PROBLEM OF THE VERY HIGH LEVEL OF ACIDIC LOADINGS TO ONTARIO'S ENVIRONMENT.

EVOLUTION OF ONTARIO'S INVOLVEMENT

AS NOTED EARLIER, RECOGNITION OF THE PROBLEM CAME AS A CONSEQUENCE OF PRECIPITATION MEASUREMENTS ASSOCIATED WITH THE SUDBURY ENVIRONMENTAL AND LAKESHORE CAPACITY STUDIES. ADDITIONAL KEY EVENTS LEADING TO THE INSTIGATION OF A MAJOR ENVIRONMENTAL PROGRAM BY THE ONTARIO MINISTRY OF THE ENVIRONMENT ARE AS FOLLOWS:

ON JUNE 21, 1977 THE HONOURABLE R. LABLANC REFERENCED THE LONG-RANGE TRANSPORT OF AIR POLLUTANTS PROBLEM IN A FORMAL ADDRESS GIVEN AT THE AIR POLLUTION CONTROL ASSOCIATION CONFERENCE WHICH WAS HELD IN TORONTO.

ON OCTOBER 21, 1977 THE ONTARIO MINISTRY OF THE ENVIRONMENT RELEASED A REPORT ENTITLED "ACIDIC PRECIPITATION IN SOUTH-CENTRAL ONTARIO: RECENT OBSERVATIONS." THIS REPORT RECEIVED WIDE-SPREAD PUBLICITY.

ON MARCH 27, 1978, THE ONTARIO MINISTRY OF THE ENVIRONMENT RELEASED ITS SUDBURY ENVIRONMENTAL STUDY REPORT ENTITLED "EXTENSIVE MONITORING OF LAKES IN THE GREATER SUDBURY AREA, 1974-1976" BY CONROY ET.AL. THIS REPORT ESSENTIALLY OUTLINES THE RESULTS OF A THREE-YEAR SAMPLING PROGRAM ON SOME 200 LAKES WITHIN A 200 KM RADIUS OF SUDBURY.

THE OUTSTANDING FEATURE OF THIS DOCUMENT WAS THAT IT INDICATED THAT ROUGHLY 20% OF THOSE LAKES WERE IN A RATHER DETERIORATED STATE WITH RESPECT TO THEIR WATER COLUMN FREE HYDROGEN ION CONCENTRATION AND AN ADDITIONAL 50% WERE CATEGORIZED AS BEING VERY VULNERABLE.

ON JUNE 7, 1978, A KEY TURNING POINT IN THE INSTIGATION OF INVESTIGATIONS WITH RESPECT TO THIS PHENOMENON OCCURRED AS A CONSEQUENCE OF AN ARTICLE IN THE TORONTO STAR ENTITLED "RAIN OF POLLUTION KILLING RESORT LAKES." THIS ARTICLE WAS BASED ON DATA PRESENTED IN A PAPER GIVEN AT THE GREAT LAKES MEETING BY MR. W. SCHEIDER, AN ONTARIO MINISTRY OF THE ENVIRONMENT EMPLOYEE, IN MAY, 1978.

IN JULY OF 1978, THE ONTARIO MINISTRY OF THE ENVIRONMENT REVOKED THE INCO CONTROL ORDER GIVING INCO A FOUR-YEAR REPRIEVE. THIS WAS FOLLOWED BY THE INSTIGATION OF THE ACIDIC PRECIPITATION IN ONTARIO STUDY IN OCTOBER 1978.

IN NOVEMBER OF 1978, THE BILATERAL RESEARCH CONSULTATION GROUP WAS FORMED AS A PART OF THE FEDERAL GOVERNMENT'S RECOGNITION OF THE LONG-RANGE TRANSPORT OF AIR POLLUTANTS PHENOMENON.

IN FEBRUARY OF 1979, A PRESENTATION WAS MADE TO THE

LEGISLATURE OF THE PROVINCE OF ONTARIO STANDING COMMITTEE ON RESOURCES DEVELOPMENT. THIS WAS A PRESENTATION ON ACIDIC PRECIPITATION AND ABATEMENT OF EMISSIONS FROM INCO OPERATIONS AT SUDBURY. THE RECOMMENDATIONS OF THIS COMMITTEE WERE PUBLISHED IN JUNE 1979 AND LATER REVISED IN FINAL FORM AND PUBLISHED IN OCTOBER 1979.

ON JULY 26, 1979, CANADA AND THE U.S. SIGNED A JOINT STATEMENT AGREEING TO DEVELOP A COOPERATIVE BILATERAL AGREEMENT ON AIR QUALITY. THIS WAS FOLLOWED IN OCTOBER 1979 BY THE RELEASE OF THE FIRST CANADA/U.S. BILATERAL RESEARCH REPORT ENTITLED "THE LRTAP PROBLEM IN NORTH AMERICA: A PRELIMINARY OVERVIEW."

ON OCTOBER 25, 1979 A STATEMENT ON ACIDIC PRECIPITATION TO THE LEGISLATIVE ESTIMATES COMMITTEE WAS MADE BY THE HONOURABLE HARRY PARROTT.

ON NOVEMBER 1, 2, AND 3, 1979, AN INTERNATIONALLY RECOGNIZED SEMINAR ON ACIDIC PRECIPITATION WAS HELD IN TORONTO. THIS SEMINAR, MORE THAN ANY OTHER SINGLE EVENT, HIGHLIGHTED THE INTERNATIONAL SIGNIFICANCE, INTEREST, AND RECOGNITION GIVEN THIS PROBLEM. OVER 700 ATTENDEES FROM MANY COUNTRIES AS WELL AS CANADA AND THE U.S. PARTICIPATED ACTIVELY.

ON JANUARY 18, 1980, THE HONOURABLE HARRY PARROTT MET WITH MR. D. COSTLE AND THE HONOURABLE JOHN FRASER TO DISCUSS A WORKING AGREEMENT ON ACID RAIN. THIS ACTIVITY FINALLY CULMINATED IN THE SIGNING OF A MEMORANDUM OF INTENT WITH THE ESTABLISHMENT, ON AUGUST 5, 1980, OF FIVE WORKING GROUPS WITH VERY STRINGENT DEADLINES. ONTARIO HAS REPRESENTATION ON ALL FIVE GROUPS, INrecognition of its technical expertise and historically active role.

ELEMENTS OF APPROACH

THE PROBLEM THEN, IS THE INCREASED FREE HYDROGEN ION CONCENTRATION IN PRECIPITATION WHICH IS BELIEVED TO BE ASSOCIATED WITH EMISSIONS OF OXIDES OF SULPHUR AND NITROGEN.

IN ORDER TO DEAL WITH THIS PROBLEM, THE ONTARIO MINISTRY OF THE ENVIRONMENT ESTABLISHED THREE COMMITTEES. THEY ARE THE STEERING, SCIENTIFIC AND ECONOMIC STUDIES COMMITTEES. THE STEERING COMMITTEE IS RESPONSIBLE FOR OVERALL STUDY, STRATEGY AND POLICY RECOMMENDATIONS. THE SCIENTIFIC AND ECONOMIC STUDIES MANAGEMENT COMMITTEES ARE RESPONSIBLE FOR DESIGNING AND IMPLEMENTING SPECIFIC STUDIES. THE OBJECTIVE IS TO "PROTECT THE ENVIRONMENT."

THE PROCESS OF PROBLEM DEFINITION TO GOVERNMENT POLICY IS REPRESENTED DIAGRAMMATICALLY IN FIGURE ONE.

IN ORDER TO SIMPLIFY THE APPROACH TO THIS VERY COMPLEX PHENOMENON, THE STEERING COMMITTEE ESTABLISHED FIVE MAJOR DIVISIONS OF STUDY. THEY ARE:

(I) SOURCES

(II) METEOROLOGY

(III) DEPOSITION

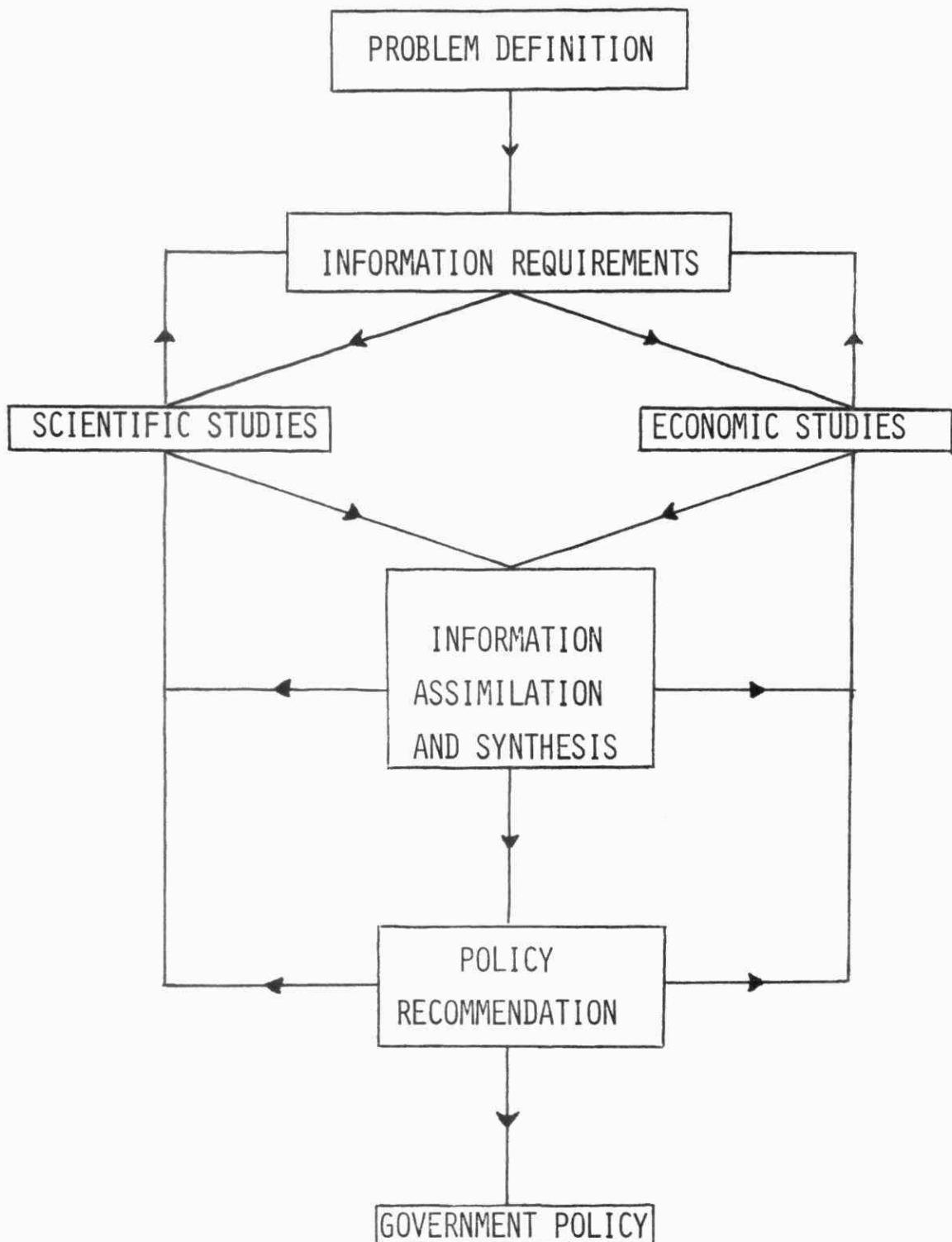


FIGURE ONE

(iv) EFFECTS

PRIMARY - AQUATIC AND TERRESTRIAL

SECONDARY - AESTHETICS, SUCH AS VISIBILITY

IMPEDIMENT, MATERIALS AND HUMAN
HEALTH

(v) SOCIO-ECONOMIC ASPECTS

SOURCES

FIGURE TWO PRESENTS EASTERN NORTH AMERICAN SO_2 EMITTING GEOGRAPHICAL AREAS. THESE GEOGRAPHICAL AREAS ARE DEFINED ON GRIDS OF 160×160 KM. THE U.S. EMISSION RATES ARE FROM THE SURE II DATA BASE 1977-1978 EMISSION RATES FOR POINT SOURCES, AND 1973-1977 EMISSION RATES FOR AREA SOURCES. CANADIAN DATA ARE FROM ENVIRONMENT CANADA AND ARE ESTIMATED 1977 EMISSION RATES FOR MAJOR SO_2 POINT SOURCES AND 1974 EMISSION RATES FOR OTHER POINT SOURCES AND AREA SOURCES.

THIRTEEN GEOGRAPHICAL AREAS ARE LISTED IN ORDER THAT THE NORANDA, QUEBEC OPERATIONS COULD BE INCLUDED. TABLE TWO LISTS THE GEOGRAPHICAL AREAS WITH THEIR RESPECTIVE EMISSION QUANTITIES. THE MOST IMPORTANT SOURCES OF OXIDES OF SULPHUR ARE THE NON-FERROUS SMELTING INDUSTRIES, 2.2×10^6 TONNES/YR., AND OTHER INDUSTRIAL PROCESSES, 1.1×10^6 TONNES/YR. (ALTSCHULLER AND McBEAN, 1979 - SEE BIBLIOGRAPHY)

IN FIGURE THREE, SIMILAR EMISSIONS ARE LISTED FOR OXIDES OF NITROGEN. THE TORONTO AREA RANKS AS #9. THE PRIMARY SOURCES OF NO_x IN EASTERN CANADA ARE FROM AUTOMOBILES - 1.2×10^6 TONNES/YR. WITH UTILITY COMBUSTION MAKING UP APPROXIMATELY 0.2×10^6 TONNES/YR. (ALTSCHULLER AND McBEAN, 1979).

TABLE THREE SIMILARILY LISTS THE MAJOR NO_X GEOGRAPHICAL AREAS.

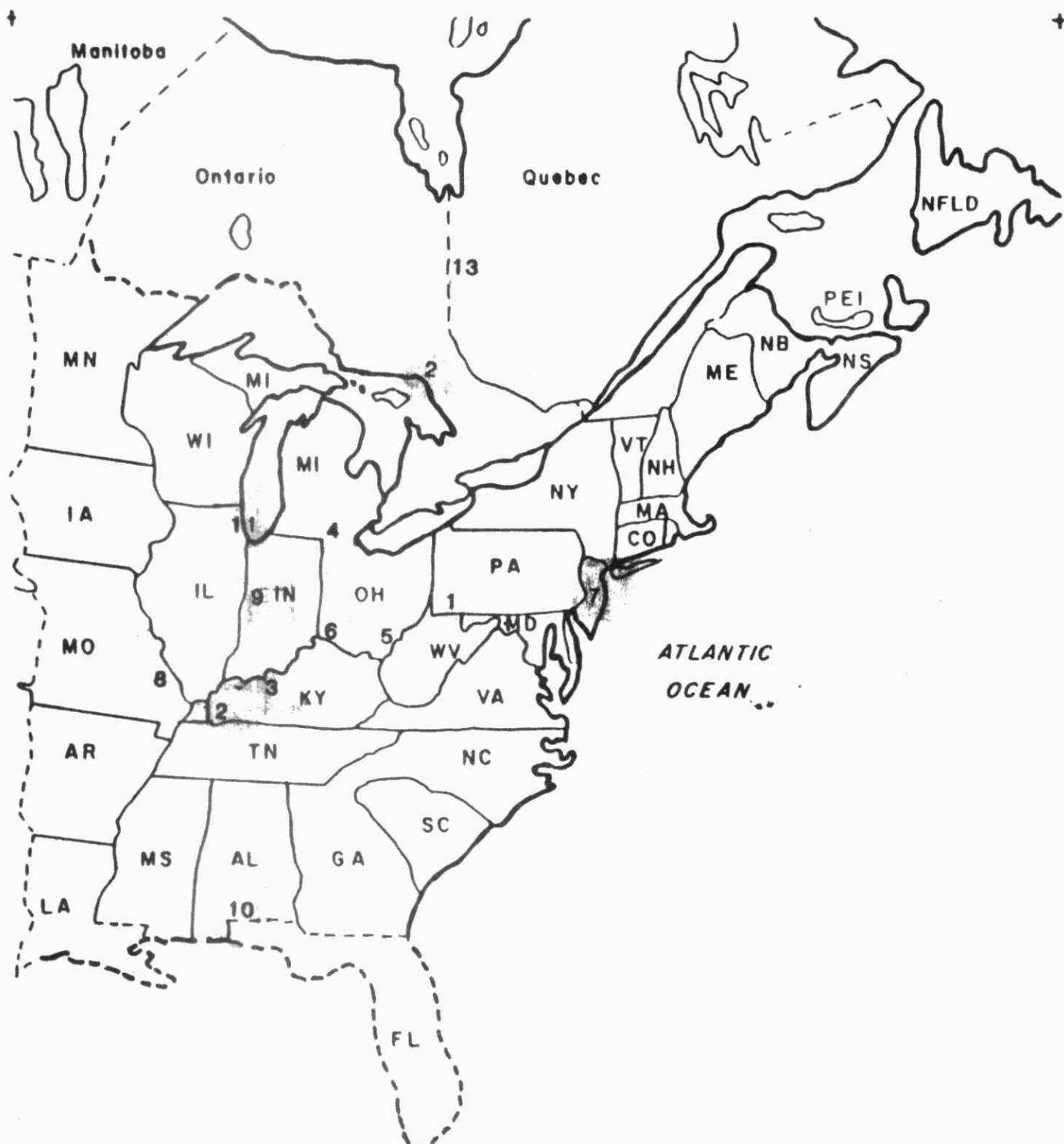
MAJOR SO₂ EMITTING GEOGRAPHICAL AREAS

FIGURE TWO

EASTERN NORTH AMERICA - MAJOR SO₂ EMITTING GEOGRAPHICAL
AREAS*

<u>GEOGRAPHICAL AREA</u>	<u>GRAMS/SECOND**</u>
1. East and West Pittsburgh; Ohio River Valley; W. Virginia	75,586.0
2. Sudbury, Ontario	43,617.8
3. W. Kentucky; Louisville; S. Indiana	41,462.5
4. Toledo, Ohio; Detroit, Michigan	40,117.7
5. Lower and Central Ohio River Valley; W. Virginia (Clarksburg)	33,863.8
6. East and West Cincinnati; Northern Kentucky	33,514.4
7. New York; New Jersey	29,868.1
8. West Illinois; East Missouri	29,514.9
9. Indianapolis, Indiana	23,507.3
10. Mobile, S. Alabama	23,352.5
11. Chicago, Illinois	22,173.7
12. Western Kentucky	21,281.2
13. Rouyn-Noranda, Quebec	16,336.0

* Geographical Area is defined as 160 km x 160 km grid square.

** The U.S. emission rates are from the SURE II data base and are 1977-78 emission rates for point sources, and 1973-77 emission rates for area sources. Canadian data are from Environment Canada and are estimated 1978 emission rates for major SO₂ point sources, and 1974 emission rates for other point sources and area sources.

30,000 gm/sec. ≈ 1MM Tons/yr.

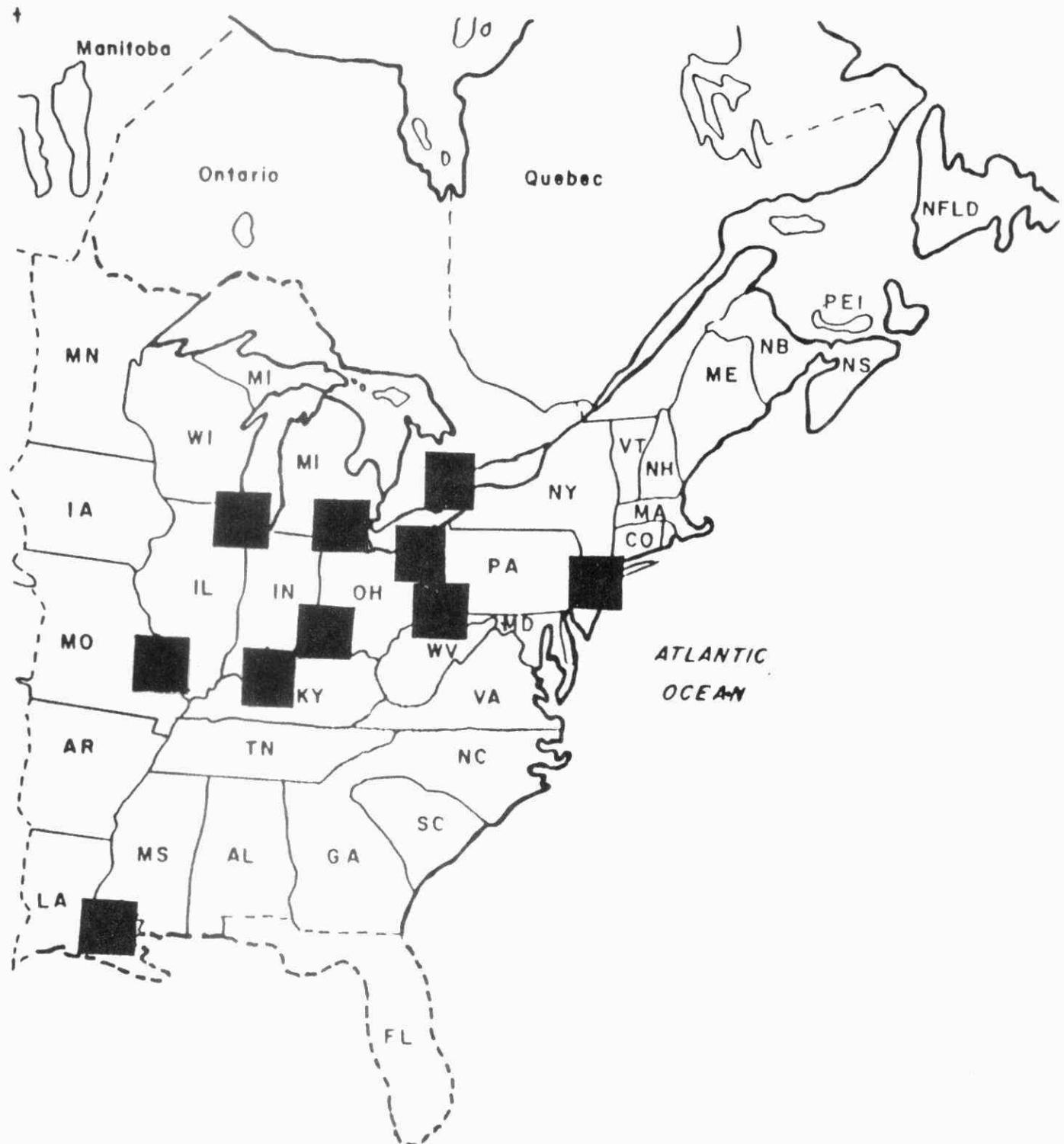
MAJOR NO_X EMITTING GEOGRAPHICAL AREAS

FIGURE THREE

EASTERN NORTH AMERICA - MAJOR NO_X EMITTING GEOGRAPHICAL
AREAS*

<u>GEOGRAPHICAL AREA</u>	<u>GRAMS/SECOND**</u>
1. New York; New Jersey	52,024.1
2. Chicago, Illinois	30,867.0
3. Toledo, Ohio; Detroit, Michigan	25,303.9
4. East and West Pittsburgh; Upper and Central Ohio River Valley	23,132.7
5. Cincinnati, Ohio; Northern Kentucky	16,536.6
6. Cleveland, Ohio; West Pennsylvania	15,541.0
7. West Kentucky; South Indiana	12,161.2
8. East Missouri; West Illinois	11,783.9
9. Toronto, Ontario	11,078.1
10. South Louisiana	10,117.8

* Geographical Area is defined as 160 km x 160 km grid square.

** The U.S. emission rates are from the SURE II data base and are 1977-78 emission rates for point sources, and 1973-77 emission rates for area sources. Canadian data are from Environment Canada and are estimated 1978 emission rates for major SO₂ point sources, and 1974 emission rates for other point sources and area sources.

30,000 gm/sec. ≈ 1MM Tons/yr.

TABLE THREE

THE RELATIONSHIP BETWEEN EMISSIONS OF OXIDES OF SULPHUR AND NITROGEN AND THE RESULTANT PRECIPITATION ACIDITY IS NOT KNOWN. HOWEVER, IT IS REASONABLE TO CONCLUDE THAT THERE IS A 1:1 RELATIONSHIP BETWEEN TOTAL EMISSION QUANTITY AND THE ULTIMATE ACIDITY OF PRECIPITATION, AT LEAST TO A FIRST APPROXIMATION. CONSEQUENTLY, FIGURE FOUR COMBINES EMISSIONS OF SO_2 AND NO_x . IN THIS MANNER, THE CANADIAN EMISSIONS RANK 8TH, 14TH AND 15TH RESPECTIVELY, THEREBY POINTEDLY DEMONSTRATING THE SIGNIFICANCE OF CONTINENTAL SOURCES AS THEY RELATE TO THIS PROBLEM.

FINALLY, TABLE FOUR COMBINES AND RANKS THE DATA FROM TABLES TWO AND THREE (PRESENTED IN FIGURE FOUR).

THE SIGNIFICANCE OF THE DISTRIBUTION OF SIGNIFICANT SOURCES WILL BECOME MORE OBVIOUS WHEN THE METEOROLOGICAL ASPECTS OF THIS PROBLEM ARE OUTLINED.

TURNING NOW TO ONTARIO, TABLE FIVE LISTS THE TEN MAJOR EMISSION SOURCES FROM THE ONTARIO INVENTORY INFORMATION SYSTEM FOR 1978. THE EMISSIONS FOR INCO ARE REDUCED SUBSTANTIALLY OVER NORMAL EMISSIONS AS 1978 WAS A STRIKE YEAR. IN ADDITION, NOTE THAT THE BRACKETED LEVEL OF 1.137 M TONNES IS IN FACT THE CURRENT EMISSION LEVEL ALLOWED UNDER THE NEW REGULATION ISSUED TO INCO ON AUGUST 28, 1980.

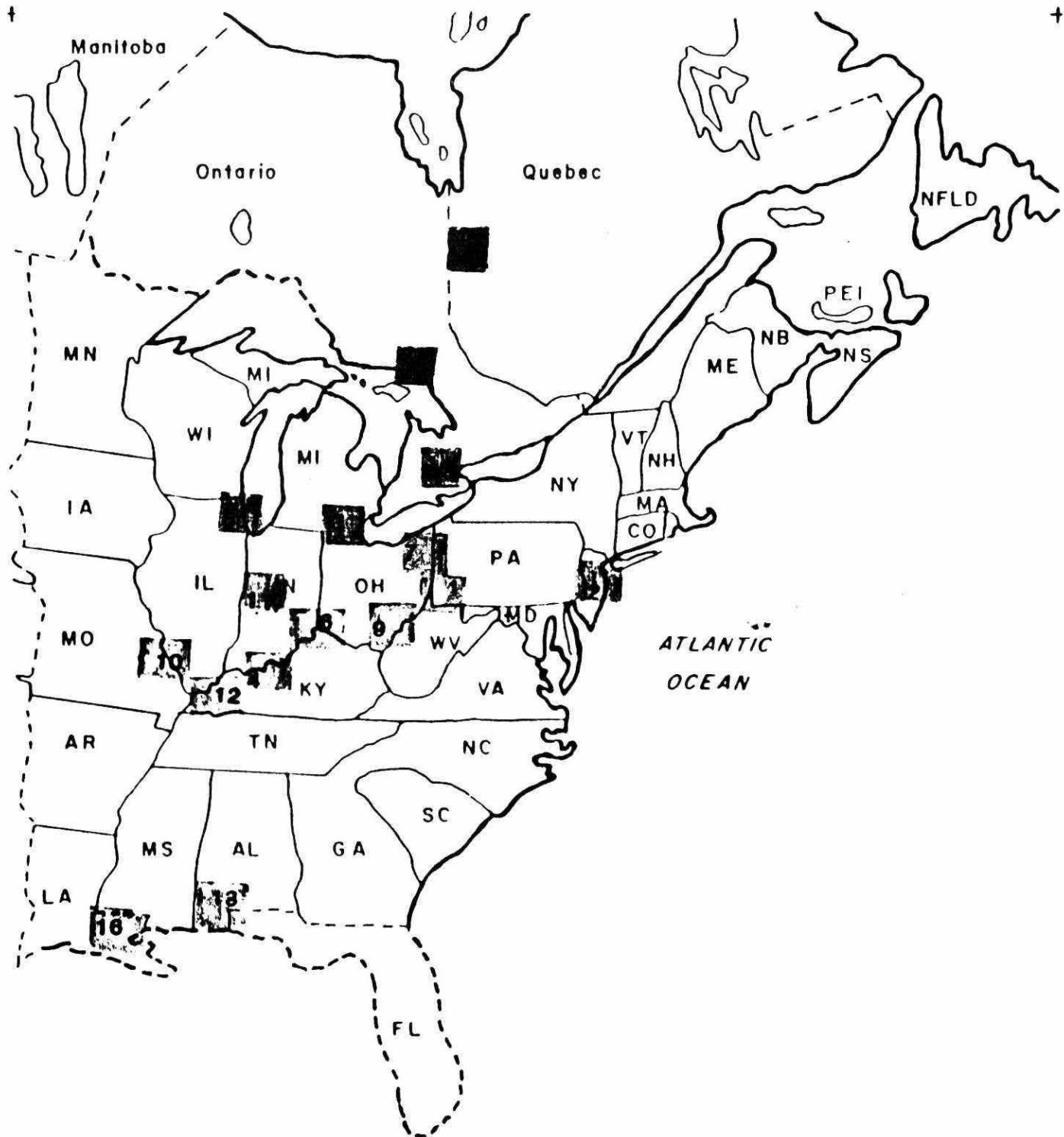
MAJOR SO₂ AND NO_X EMITTING GEOGRAPHICAL AREAS

FIGURE FOUR

EASTERN NORTH AMERICA - MAJOR SO₂ AND NO_X EMITTING
GEOGRAPHICAL AREAS*

<u>GEOGRAPHICAL AREA</u>	<u>GRAMS/SECOND**</u>
1. East and West Pittsburgh; Upper and Central Ohio River Valley	98,718.7
2. New York; New Jersey	81,892.2
3. Toledo, Ohio; Detroit Michigan	65,421.6
4. Western Kentucky; South Indiana	53,623.7
5. Chicago, Illinois	53,040.7
6. Cincinnati, Ohio; North Kentucky	50,051.0
7. Cleveland, Ohio; West Pennsylvania	47,997.7
8. Sudbury, Ontario	43,915.3
9. Lower and Central Ohio River Valley; Clarksburg, Virginia	42,401.3
10. East Missouri; West Illinois	41,298.8
11. Indianapolis, Indiana	30,202.9
12. Western Kentucky	25,849.3
13. Mobile; South Alabama	24,138.5
14. Toronto, Ontario	18,584.7
15. Rouyn - Noranda, Quebec	16,402.2
16. Southern Louisiana	14,596.8

* Geographical Area is defined as 160 km x 160 km grid square.

** The U.S. emission rates are from the SURE II data base and are 1977-78 emission rates for point sources, and 1973-77 emission rates for area sources. Canadian data are from Environment Canada and are estimated 1978 emission rates for major SO₂ point sources, and 1974 emission rates for other point sources.

30,000 gm/sec. ≈ 1MM Tons/yr.

ONTARIO SO₂ EMISSION 1978
 10 MAJOR EMISSION SOURCES
 IN THE ONTARIO INVENTORY INFORMATION SYSTEM

<u>EMISSION SOURCE</u>	<u>LOCATION</u>	SO ₂ EMISSION <u>10³ TONNES/YR.</u>
1. INCO*	SUDBURY	566.99 (1,137.0)
2. NANTICOKE, G.S.	NANTICOKE	183.84
3. ALGOMA STEEL, ORE DIVISION	WAWA	163.29
4. LAMBTON, G.S.	SARNIA	130.89
5. FALCONBRIDGE SMELTER**	SUDBURY	117.03 (200.0)
6. LAKEVIEW, G.S.	TORONTO	89.25
7. IMPERIAL OIL LTD.	SARNIA	28.85
8. LENNOX, G.S.	BATH	21.30
9. STELCO LTD.	HAMILTON	16.91
10. ALGOMA STEEL CORP. LTD.	SAULT STE. MARIE	<u>14.41</u>
		1332.76 (1,985.74)

* STRIKE YEAR; INCO 1977 ANNUAL SO₂ EMISSION 2506.6×10^6 LB/YR.
 - $1.137 \text{ TONNES} \times 10^6/\text{YR.}$

** PRODUCTION CUT BACK; FALCONBRIDGE SMELTER 1977 SO₂ EMISSION
 440.9×10^6 LB/YR.
 - 200×10^3 TONNES/YR.

THE EMISSIONS FROM INCO OPERATIONS IN SUDBURY CONSTITUTE THE MOST SIGNIFICANT SINGLE-POINT SOURCE OF SO_2 EMISSIONS ON THE CONTINENT. HOWEVER, IN ONTARIO, THE SECOND-MOST SIGNIFICANT SOURCE OF SO_2 IN A COLLECTIVE MANNER AND A SIGNIFICANT SOURCE OF NO_x , ARE THE OPERATIONS OF ONTARIO HYDRO.

TABLE SIX LISTS ONTARIO HYDRO'S SO_2 AND NO_x EMISSIONS FOR 1979.

DEPOSITION

THE TRANSFER OF ACIDIC MATERIALS FROM THE ATMOSPHERE TO THE ENVIRONMENT IS CALLED DEPOSITION. THE MAJOR DIVISIONS ARE DRY GASEOUS, DRY PARTICULATE, AND ALL FORMS OF PRECIPITATION.

ONTARIO HYDRO SO₂ AND NO_X EMISSIONS FOR 1979

STATION	SO ₂ (MG/YEAR)	NO _X *(MG/YEAR)
WINDSOR	31	10
THUNDER BAY	10,033	1,059
R L HERNE	10,191	4,291
LAKEVIEW	91,347	13,785
LAMBTON	160,249	12,864
NANTICOKE	155,078	28,650
LENNOX	10,012	992
TOTALS	436,941	61,651
	(480,000)**	(68,000)**

* NO_X EXPRESSED AS NO

** TONS/YEAR

1980: PREDICTED LEVELS WILL BE DOWN SLIGHTLY

EFFECTS

THE PRIMARY EFFECTS OF GREATEST CONCERN ARE TO THE AQUATIC BIOSPHERE AS IT IS THE MOST SUSCEPTIBLE TO ADVERSE EFFECTS FROM ACIDIC LOADINGS. SPORT FISHERIES, SUCH AS THE BROOK AND LAKE TROUT, ARE THE MOST SENSITIVE TO ACIDIFICATION OF THEIR HABITATS. THESE FISHERIES ARE AFFECTED BY BOTH THE GRADUAL ACIDIFICATION OF THEIR ENVIRONMENT AND THE SO-CALLED "SPRING SHOCK" LOADING, THAT IS, THE SUDDEN RELEASE OF FREE HYDROGEN IONS DURING SPRING RUNOFF.

LAKE AND WATERSHED SUSCEPTIBILITY TO ACIDIFICATION IS DIRECTLY RELATED TO THE LACK OF BUFFERING MATERIALS LIKE CaCO_3 IN A LAKE'S DRAINAGE BASIN. THIS LACK OF BUFFERING CAPACITY IS PROMINENT IN MANY RECREATIONALLY IMPORTANT AREAS OF ONTARIO.

TERRESTRIAL EFFECTS, WHICH INCLUDE SOILS AND VEGETATION, ARE CONTROVERSIAL AT THIS TIME. THERE IS EVIDENCE TO SHOW BENEFICIAL, AS WELL AS DETRIMENTAL, CONSEQUENCES OF INCREASED ACIDIC LOADINGS. THE ULTIMATE RESOLUTION TO THIS QUESTION WILL REQUIRE MANY ADDITIONAL YEARS OF RESEARCH.

SECONDARY EFFECTS SUCH AS VISIBILITY IMPEDIMENT AND MATERIAL DAMAGES ARE OTHER AREAS OF CONCERN AND CONTROVERSY. AGAIN, ADDITIONAL INVESTIGATIVE RESEARCH WILL HAVE TO BE

UNDERTAKEN BEFORE THE FINAL VERDICT WILL BE CLEAR TO ALL.

FINALLY, HEALTH EFFECTS, WHICH ARE RELATED TO SULPHATE INHALATION, ARE ALSO VERY CONTROVERSIAL. DATA ARE VERY SPARSE AND IRRESOLVABLE, FROM THE CURRENT VANTAGE POINT, BUT CERTAINLY DESERVING OF ADDITIONAL ATTENTION.

SOCIO-ECONOMIC ASPECTS

IN ORDER TO DEVELOP A RATIONAL APPROACH TO THE SOLUTION OF THE PROBLEM, IT IS NECESSARY TO BE ABLE TO QUANTIFY THE COSTS OF POLLUTION CONTROL AS WELL AS THE ENVIRONMENTAL BENEFITS WHICH WILL RESULT. AS WITH THE OTHER DIVISIONS, THERE ARE MANY UNANSWERABLE QUESTIONS AT THIS TIME. HOWEVER, THE ANSWERS TO QUESTIONS OF ECONOMIC IMPACT WILL BE INSTRUMENTAL IN CATALIZING SOCIETY INTO HAVING THE WILL TO DEAL WITH THIS COMPLEX PHENOMENON.

ONTARIO'S PROGRAM

THE ACIDIC PRECIPITATION IN ONTARIO STUDY'S BUDGET FOR FISCAL 1980/1981 IS APPROXIMATELY FIVE MILLION DOLLARS. THE ONTARIO MINISTRY OF THE ENVIRONMENT HAS FOUR MILLION OF THESE FUNDS AND THE ONTARIO MINISTRY OF NATURAL RESOURCES HAS ONE MILLION. THE FOLLOWING CONSTITUTES A SUMMARY OF THE AREAS OF CONCENTRATED ACTIVITY AT THIS PARTICULAR TIME. THE MAIN DIVISIONS ARE IDENTICAL TO THOSE DISCUSSED IN THE PREVIOUS SECTION.

SOURCES

THE INTENT OF THIS ACTIVITY IS TWO-FOLD:

- 1) TO DESIGN A SYSTEM TO PROVIDE EMISSION DATA HANDLING TO ASSIST IN THE PREPARATION FOR EMISSION QUANTITIES FOR INPUT INTO THE LONG-RANGE TRANSPORT MODELS.
- 2) TO DEVELOP AND IMPLEMENT A COMPUTERIZED INFORMATION SYSTEM WHICH WILL HANDLE THE DATA COLLECTED UNDER 1).

THE VAST NUMBER OF INDIVIDUAL SOURCES ON A CONTINENTAL SCALE, COUPLED WITH THE FACT THAT THERE ARE A MYRIAD OF MEANS OF QUANTIFYING EMISSION SOURCES, PLUS THE NUMEROUS AGENCIES, PROVINCIAL, STATE, AND FEDERAL, MAKES THE COLLECTION OF A STANDARDIZED INVENTORY OF EMITTANTS A DIFFICULT TASK. EFFORTS ARE CURRENTLY UNDERWAY TO STANDARDIZE ASSOCIATED METHODOLOGIES.

METEOROLOGY

METEOROLOGY INCLUDES ATMOSPHERIC MODELLING AND THE COLLECTION AND COMPILATION OF A VAST QUANTITY OF WEATHER STATISTICS. UNDER THE MODELLING ASPECT OF THIS ACTIVITY, WORK WILL BE CONTINUED ON THE VALIDATION OF CURRENTLY DEVELOPED STATISTICAL MODELS AND INVESTIGATION OF THE APPROPRIATENESS AND APPLICABILITY OF OTHER KINDS OF MODELS SUCH AS THE LAGRANGIAN MODEL. THE ULTIMATE AIM OF THIS ACTIVITY IS TO MODEL SOURCE-RECEPTOR LINKAGES SUCH THAT THE RESULTS OF ABATEMENT ACTIVITIES CAN BE PREDICTED BEFORE THE EXPENSE OF ACTUAL ABATEMENT BEGINS. THE IMPORTANCE OF MODELLING HAS BEEN HIGHLIGHTED BY THE RECENT MEMORANDUM OF INTENT SIGNED BY THE GOVERNMENTS OF CANADA AND THE U.S. ONTARIO HAS REPRESENTATION ON THIS GROUP AND TO DATE, HAS MAINTAINED A VERY HIGH PROFILE, DUE TO THE INTERNATIONALLY RECOGNIZED EXPERTISE OF ITS SCIENTISTS. AGREEMENT BY U.S. AND CANADIAN AUTHORITIES AS TO THE APPROPRIATENESS OF A SPECIFIC MODEL OR MODELS, WILL BE THE MOST SIGNIFICANT FORERUNNER TO A TREATY BETWEEN THE TWO COUNTRIES WHICH IS IMPERATIVE IF THIS PROBLEM IS TO BE SUCCESSFULLY RESOLVED.

DEPOSITION

AS INDICATED EARLIER, MATERIAL IS TRANSFERRED FROM THE ATMOSPHERE TO THE ENVIRONMENT VIA SEVERAL MECHANISMS. THESE MECHANISMS INCLUDE DRY GASEOUS, DRY PARTICULATE AND PRECIPITATION IN ALL FORMS. IN ORDER TO MEASURE, QUANTIFY AND ULTIMATELY IDENTIFY SPECIFIC SOURCES OF THESE MATERIALS, ONTARIO HAS SET UP TWO INDEPENDENT NETWORKS.

THE CUMULATIVE NETWORK: AT PRESENT, ONTARIO HAS OPERATING THROUGHOUT THE PROVINCE SOME 33 MONTHLY CUMULATIVE WET AND DRY MONITORS. THE MAJOR FUNCTION OF THESE MONITORS IS TO MEASURE, ON A PROVINCIAL BASIS, THE ENVIRONMENTAL LOADING OF ACIDIFYING MATERIALS. THIS WILL ALLOW US TO QUANTIFY AND DRAW UP LOADING ISOPLETHS FOR ALL AREAS OF THE PROVINCE.

EVENT NETWORK: THIS NETWORK CONSISTS OF MONITORS FROM WHICH SAMPLES WILL BE COLLECTED ON A DAILY, THAT IS, A 24-HOUR BASIS. IT IS CURRENTLY PLANNED THAT THERE WILL BE THREE SUCH STATIONS CONSISTING OF FIVE MONITORS LOCATED WITHIN A 50 KM RADIUS. THE CURRENT PROPOSED LOCATIONS ARE: KINGSTON, DORSET, AND LONDON. THE MAJOR FUNCTION OF THIS NETWORK WILL BE TO RELATE, USING METEOROLOGY AND THE MODELLING ACTIVITY, THE SIGNIFICANCE OF SPECIFIC SOURCES AS THEY IMPACT UPON SPECIFIC RECEPTORS, FIRST ON A CONTINENTAL BASIS AND THEN ULTIMATELY ON A PROVINCIAL LEVEL.

EFFECTS

AS PREVIOUSLY STATED, THE MOST OBVIOUS AND WIDELY DISCUSSED AREA OF DETRIMENTAL EFFECT IS TO THE AQUATIC BIOSPHERE. THIS IS A CONSEQUENCE OF THE FACT THAT A GREAT DEAL OF THE EASTERN NORTHERN AMERICAN CONTINENTAL ENVIRONMENT IS DEFICIENT IN BUFFERING MATERIALS. MANY STREAMS, RIVERS AND LAKES (TOTAL WATERSHEDS) ARE THEREFORE, QUITE SUSCEPTIBLE TO ACIDIC LOADINGS.

AT THIS PARTICULAR TIME, ONTARIO HAS BEEN DEALING WITH THIS PROBLEM ON A PROVINCIAL SCALE. ACTIVITIES TO SAMPLE AS MANY LAKES AS POSSIBLE IN THE PROVINCE ARE WELL UNDERWAY. SENSITIVE LAKES ARE BEING IDENTIFIED AND CLASSIFIED AND SOME OF THEM ARE BEING INCORPORATED INTO INTENSIVE CALIBRATED WATERSHED STUDIES. THESE INTENSIVE STUDIES INCLUDE ALL ASPECTS, FROM THE MEASUREMENT OF SPECIFIC LOADINGS, THE QUANTIFICATION OF EFFECTS ON THE TERRESTRIAL BIOSPHERE, AND ULTIMATELY, TO THE ACIDIC INPUT TO LAKES. IN PARTICULAR, DETAILED MEASUREMENT AND BUDGETING OF MATERIAL INPUTS TO AND FROM THE LAKE AND THE ULTIMATE CREATION OF RECEPTOR-EFFECTS MODELS, IS THE OBJECTIVE. THESE MODELS, TOGETHER WITH THE ATMOSPHERIC METEOROLOGICAL MODELS, WILL ULTIMATELY ALLOW THE QUANTIFICATION OF THE SIGNIFICANCE OF CHANGES IN EMISSIONS ON A CONTINENTAL BASIS. IN THE ULTIMATE MODEL, IT WILL BE POSSIBLE TO PREDICT THE ENVIRONMENTAL SIGNIFICANCE OF CHANGES IN THE MORE IMPORTANT SINGULAR SOURCES.

TERRESTRIAL INVESTIGATIONS CONSIST OF THE FOLLOWING ACTIVITIES: MAPPING OF SOIL AND VEGETATION SENSITIVITIES ON A PROVINCIAL SCALE, THE ESTABLISHMENT OF BASELINE SOIL AND VEGETATION DATA AND THE ESTABLISHMENT OF PERMANENT SAMPLE PLOTS ON A PROVINCIAL BASIS. IN ADDITION, LABORATORY STUDIES WHICH ARE USING SIMULATED ACID RAIN OF VARYING CONCENTRATIONS ARE UNDERWAY. THIS ALLOWS THE COMPRESSION OF THE NATURALLY OCCURRING TIMEFRAME AND ASSISTS IN ELUCIDATING THE TEMPORAL ASPECT OF THIS PROBLEM AS IT RELATES TO IMPORTANT CROPS.

A GREAT DEAL OF WORK IS CURRENTLY UNDERWAY, TO DEAL WITH THE ASPECTS OF MATERIAL DAMAGE, AESTHETICS IMPEDIMENT, AND HUMAN HEALTH EFFECTS FROM THIS PHENOMENON. ONTARIO HAS INTEGRATED, WHERE POSSIBLE AND APPROPRIATE, ITS ACTIVITIES TO A HIGH DEGREE WITH INDEPENDENT ACADEMIC STUDIES AND FEDERAL INVESTIGATIVE AGENCIES.

SOCIO-ECONOMIC ACTIVITIES

SOCIO-ECONOMIC ACTIVITIES FORM AN INTEGRAL PART OF THE ACIDIC PRECIPITATION IN ONTARIO STUDY. IN THE ULTIMATE SELECTION OF POLICY RECOMMENDATIONS, IT WILL BE IMPERATIVE TO HAVE DETAILED, QUANTITATIVE COST-BENEFIT DATA ON THE IMPACT OF THIS PHENOMENON ON ONTARIO'S ECONOMY. IN ORDER TO ASSIST IN THE ACQUISITION OF THE NECESSARY INFORMATION, THE ONTARIO MINISTRY OF THE ENVIRONMENT, ACTING AS THE LEAD AGENCY, HAS INTEGRATED ACTIVITIES WITH THE FOLLOWING MINISTRIES: THE MINISTRY OF NATURAL RESOURCES, THE MINISTRY OF INDUSTRY AND TOURISM, THE MINISTRY OF ENERGY, THE MINISTRY OF AGRICULTURE AND FOOD, AND THE MINISTRY OF TREASURY AND ECONOMICS. THESE MINISTRIES, TOGETHER, HAVE CATALOGUED ACTIVITIES UNDER THE FOLLOWING GUIDELINES:

- 1) ENUMERATION OF PHYSICAL EFFECTS IN ORDER TO ESTIMATE THEIR VALUE IN DOLLARS;
- 2) DETERMINATION OF PUBLIC ATTITUDES AND WILLINGNESS TO PAY;
- 3) DEVELOPMENT OF ABATEMENT COST FUNCTIONS FOR SO_2 AND NO_x ;
- 4) INVESTIGATION OF INTERIM MITIGATIVE COSTS AND EFFECTIVENESS;

5) EXPLORATION OF POLICY INSTRUMENTS AND OPTIONS FOR ABATEMENT.

A GREAT DEAL OF ACTIVITY HAS BEEN UNDERWAY DURING THIS FISCAL YEAR AND CONTRACTS HAVE BEEN LET FOR THE FOLLOWING SPECIFIC STUDIES:

TOURISM AND RECREATION STUDY - THIS STUDY IS CURRENTLY BEING CARRIED OUT BY CURRIE, COOPERS AND LYBRAND LTD, AND WILL GENERATE ESTIMATES OF THE IMPACTS OF ACID RAIN ON TOURISM AND RECREATION EXPENDITURES INCLUDING THE JOBS DEPENDENT ON THAT SECTION;

AMENITY VALUE SURVEY STUDY - THIS STUDY IS BEING DESIGNED BY A.R.A. CONSULTANTS OF TORONTO AND WILL MORE CLEARLY DISCERN AND ESTIMATE VALUES THAT PEOPLE PLACE ON ENVIRONMENTAL AND RECREATIONAL RESOURCES WHICH ARE VULNERABLE TO ACID RAIN. THIS SURVEY IS ALSO EXPECTED TO PROVIDE NEW DATA ON RECREATIONAL ACTIVITIES AND WILL BE CARRIED OUT DURING THE SUMMER OF 1981;

FINANCIAL VALUE STUDY - THIS STUDY WILL FOCUS ON THE ACTUAL POTENTIAL EFFECTS ON SECTORS IN THE ECONOMY WHICH PRODUCE GOODS AND SERVICES FOR SALE AND FOR WHICH MARKET PRICES ARE GENERALLY AVAILABLE. COMMERCIAL FISHING, CORROSION OF STRUCTURES AND MATERIALS, EFFECTS

ON NATIVE FISHERIES, REDUCED PRODUCTION IN FORESTRY AND AGRICULTURE, ARE AMONG THE FACTORS TO BE TAKEN INTO ACCOUNT. THIS STUDY IS PRESENTLY TO GO TO TENDER.

IN ADDITION, AN ONTARIO/CANADA TASK FORCE TO STUDY SUDBURY POLLUTION ABATEMENT OPTIONS WAS ANNOUNCED BY THE ENVIRONMENT MINISTER ON AUGUST 29, 1980. THIS TASK FORCE IS PART OF THE ONTARIO CONTROL PROGRAM FOR INCO LTD., AS ANNOUNCED ON MAY 1, 1980 IN THE HOUSE BY THE HONOURABLE HARRY PARROTT. THE TASK FORCE WILL MAKE A COMPLETE INDEPENDENT ASSESSMENT OF THE POSSIBLE TECHNOLOGIES TO FURTHER REDUCE EMISSIONS IN THE SUDBURY AREA. ITS OBJECTIVE IS TO REPORT ON THE ENVIRONMENTAL, ECONOMIC AND SOCIAL CONSEQUENCES OF ALTERNATIVE ABATEMENT OPTIONS. THE TASK FORCE IS COMPOSED OF SENIOR REPRESENTATIVES FROM THE ONTARIO MINISTRIES OF THE ENVIRONMENT AND NATURAL RESOURCES AND THE FEDERAL DEPARTMENTS OF ENVIRONMENT, AND ENERGY, MINES AND RESOURCES. IN ADDITION, ONE PUBLIC REPRESENTATIVE HAS BEEN NOMINATED BY EACH OF THESE GOVERNMENT AGENCIES.

SUMMARY

ONTARIO SCIENTISTS AND MANAGERS HAVE BEEN LEADERS IN THE AREA OF RECOGNITION AND ACTIONS AS THEY RELATE TO THIS PHENOMENON. ACTIONS TAKEN BY THE MINISTRY OF THE ENVIRONMENT TO DATE INCLUDE THE ANNOUNCEMENT OF A REGULATION, WHICH IS THE TOUGHEST MEANS AVAILABLE UNDER CURRENT LEGISLATION, TO FURTHER REDUCE INCO's EMISSIONS TO THE PRESENT LEVEL OF 2500 TONS/DAY AND WITH THE VIEW OF FURTHER REDUCTIONS TO 1950 TONS/DAY BY DECEMBER 31, 1982. IN ADDITION, ALL OTHER SOURCES IN ONTARIO ARE CURRENTLY UNDER CLOSER SCRUTINY. IN PARTICULAR, ONTARIO HYDRO IS IN THE PROCESS OF DEVELOPING A MANAGEMENT SCHEME TO DEAL WITH ITS EMISSIONS ON A PROVINCIAL BASIS. THESE PROPOSALS WILL SHORTLY BE PRESENTED FOR GOVERNMENT REVIEW AND RECOMMENDATIONS AND ULTIMATELY ACTION WILL BE FORTHCOMING. OTHER PROVINCIAL SOURCES ARE ALSO BEING CONSIDERED AND ANNOUNCEMENTS WILL FOLLOW DEALING WITH THESE SOURCES IN DUE COURSE.

AS A LARGE NUMBER OF SOURCES THAT AFFECT ONTARIO ARE OUTSIDE OF ONTARIO'S JURISDICTION, IT WILL BE NECESSARY IN THE INTERIM TO DEVELOP MEANS OF PROTECTING THOSE AREAS OF THE ENVIRONMENT THAT ARE DEEMED MOST SENSITIVE AND ECONOMICALLY IMPORTANT. TO THAT END, A MAJOR PROGRAM IS CURRENTLY BEING DEVELOPED TO EXPERIMENTALLY EXPLORE

MEANS, SUCH AS THE APPLICATION OF CALCIUM CARBONATE, TO PARTICULARLY IMPORTANT AND SUSCEPTIBLE WATERWAYS IN ORDER TO PROTECT THEM. IN ADDITION, DATA AND EXPERIENCE HAS BEEN AND WILL CONTINUE TO BE ACCUMULATED FROM THE SCANDINAVIAN AND NEW YORK EXPERIENCES WITH RESPECT TO APPLICATION OF CHEMICALS AND THE FOSTERING OF MORE TOLERANT FISH SPECIES. OTHER POSSIBILITIES FOR ALLEVIATING THIS PHENOMENON ARE ALSO BEING EXPLORED. SOME OF THESE INCLUDE WHOLE WATERSHED RE-VEGETATION, AND SO ON.

THE ONTARIO MINISTRY OF THE ENVIRONMENT, TOGETHER WITH OTHER MINISTRIES, HAS FOCUSSSED A GREAT DEAL OF ATTENTION ON THIS VERY COMPLEX PHENOMENON. NO EFFORT HAS BEEN SPARED TO EXPLORE THE SCIENTIFIC, AS WELL AS THE SOCIO-ECONOMIC ASPECTS AND A GREAT DEAL OF ENERGY HAS BEEN PUT INTO ENSURING COMMUNICATION, COOPERATION AND ULTIMATE INTEGRATION WITH OTHER AREAS OF INVESTIGATION, INCLUDING FEDERAL STUDIES. ONTARIO IS WELL REPRESENTED ON ALL THE COMMITTEES WHICH HAVE RESULTED FROM THE MEMORANDUM OF INTENT SIGNED BETWEEN THE FEDERAL AMERICAN AND CANADIAN GOVERNMENTS.

IN CONCLUSION, AS CITIZENS OF THIS PROVINCE AND COUNTRY, IT FALLS UPON US TO TAKE WHATEVER MEANS AND MEASURES ARE AVAILABLE TO HELP ALLEVIATE THIS PROBLEM. THESE MEASURES INCLUDE:

- COMMUNICATING OUR CONCERN TO ELECTED REPRESENTATIVES, BOTH FEDERALLY AND PROVINCIALL;
- INFORMING OUR FELLOW AMERICANS OF THEIR CONTRIBUTION TO THE PROBLEM AND OUR UNWILLINGNESS TO LET THIS SITUATION CONTINUE;
- MODIFYING OUR EVERYDAY ACTIVITIES TO REDUCE OUR ENERGY CONSUMPTION AND MATERIAL WASTAGE WHICH ULTIMATELY AFFECT EMISSIONS.

ONLY THROUGH THE MECHANISM OF PERSONAL COMMUNICATION AND ULTIMATE INDIVIDUAL INFLUENCE ON THE GOVERNMENTS IN BOTH COUNTRIES WILL STRONG CORRECTIVE ACTION BE TAKEN TO DEAL WITH THIS CONTEMPORARY, VERY COMPLEX, AND ENVIRONMENTALLY DEBILITATING PHENOMENON.

BIBLIOGRAPHY

1. ALTSCHULLER, A. P.; McBEAN, G. A., THE LRTAP PROBLEM IN NORTH AMERICA: A PRELIMINARY OVERVIEW, OCTOBER, 1979.
2. CONROY, ET.AL.; M.O.E. REPORT, EXTENSIVE MONITORING OF LAKES IN THE GREATER SUDBURY AREA, 1974-1976, 1978.

1986
05
172-9
TD